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THE

PHYSICAL REVIEW

AN EXPERIMENTAL INVESTIGATION OF THE ENERGY OF THE CHARACTERISTIC K-RADIATION FROM CERTAIN METALS

By Emory Carl Unnewehr

Abstract

Energy of K-radiation from Cr, Cu, Rh, and Ag, for applied voltages to 45 kv.—Using a special Coolidge tube with a thin mica window, and a rotatable anti-cathode on which were mounted four metals, the intensities of the characteristic K x-rays from Cr(atomic number 24), Cu(29), Rh(45), and Ag(47), corrected for general radiation, for incomplete absorption in ionization chamber, for incomplete reflection by crystal, and for absorption by mica window, were found to be approximately linear functions of the square of the applied voltage on the tube. The ratio of the intensities of the α and β radiations was constant for each metal and decreased regularly with increasing atomic number from 7.36 for Cr to 4.65 for Ag. The ratio of the α radiation to the general radiation also decreased, but more markedly, from 25 for Cr to 11.2 for Cu and 2.7 for Ag. *Comparison with the theory* of Bergen Davis shows good agreement for Ag and Rh, but not for Cr and Cu. This is probably due to the fact that the theory neglects the fluorescent re-emission of absorbed general radiations.

Absorption coefficient of Rh for its K-radiation was found to be 222 per cm for Kα and 178 per cm for Kβ.

Absorption coefficients of mica for K-radiation from Cr, Cu, Rh, and Ag were found to be 227, 89.2, 7.7 and 5.1 per cm, for the Kα radiation and 171, 66, 5.5 and 3.6 per cm, for the Kβ radiations of the respective metals.

THE experiments reported here are part of a systematic investigation of the energy of x-ray emission, which is now being carried forward in the Phoenix Physical Laboratory of Columbia University.

The particular object of the present experiments was the investigation of the K-characteristic emission from silver (atomic number 47), rhodium (45), copper (29) and chromium (24), under identical conditions for the purpose of comparison. These radiations were investigated for:

(a) The dependence of energy of emission upon applied voltage;

(b) The dependence of energy of emission upon the atomic number;

(c) The relation of the energy of the K-characteristic emission to the energy at that wave-length in the continuous spectrum;

(d) The ratio of the energies of the α to the β characteristic emission.

The purpose also was further to check and test a theory of characteristic x-ray emission developed by Bergen Davis.[1] This theory was developed from purely theoretical considerations after D. L. Webster[2] had shown that the energy of emission of characteristic x-radiation from a target increases rapidly with the voltage. In this theory, Bergen Davis formulated an expression for the intensity of the characteristic radiation in terms of the applied voltage. The values calculated from this theory agreed very closely with experimental results obtained by B. A. Wooten.[3]

Description of Apparatus

A motor generator set furnished current at 125 volts and 500 cycles to a 3 kw oil immersed transformer. The alternating current at high voltage was rectified by means of two General Electric kenetrons and a large condenser. Power was supplied to the x-ray tube from this condenser.

The voltage was measured by an electrostatic voltmeter. It consists of two fixed spheres and two movable spheres hung in the same plane by a steel suspension. When the spheres were charged to the same potential, there was a repulsion between the movable and fixed spheres, thus causing a deflection of the movable spheres. Before the data were taken, the voltmeter was recalibrated by means of a spark gap between two spheres which were 12.5 cm in diameter, since for such spheres tables of the relation between the length of spark gap and voltage are available, and a calibration curve was drawn. It proved to be a smooth, consistent curve. During the time during which readings were taken, the voltage was kept constant to within about one per cent.

The spectrometer was of the usual type employed, except that the ionization chamber was quite long, being 150 cm in length. The measurements were made with a gold leaf electroscope of special design attached directly to the end of the ionization chamber. In this chamber air saturated with vapor of methyl iodide was used since it shows no critical absorption in the range of frequencies obtained in this investigation. The air and vapor were kept dry by means of phosphorous pentoxide in the usual manner. The slit in the end of the ionization chamber was closed by a mica window .001 cm thick, which permitted the passage of even the softest radiation without very great absorption. The beam

[1] Davis, Phys. Rev. **11**, 433, 1918
[2] Webster, Phys. Rev. **7**, 599, 1916
[3] Wooten, Phys. Rev. **18**, 71, 1919

of x-rays was defined by two adjustable lead slits placed between the x-ray tube and the crystal.

The x-rays were deflected from a crystal of calcite which had previously been used for x-ray reflection. No flaws in the structure of the face used had been found.

The x-ray tube was of the Coolidge type and was built in this Laboratory. The filament of the Coolidge cathode was heated by current from a small storage battery. The target consisted of a hexagonal copper cylinder, on the faces of which the other metals whose radiations were examined were mounted. These metals were placed so that the faces upon which the electrons struck were at exactly equal distances from the axis. The target was supported on a pivot which was securely anchored to the bottom of the x-ray tube. The hexagonal target could be rotated about the axis by a suitable magnet placed outside the x-ray tube. By this means, it was possible to bring any of the four metals into the same position with respect to the slit and to the Coolidge cathode.

Besides the rotating target, the x-ray tube had one other interesting feature. In the side of the x-ray tube toward the spectrometer, a hollow steel cylinder was fitted into the glass by means of a ground glass joint sealed with DeKotinsky cement. In the end of this cylinder was a narrow window about 2 mm wide and 2 cm high. This window was covered with a thin sheet of mica, 0.0014 cm thick. The small absorption in this mica window could easily be calculated.

Description of Method

The apparatus was first carefully put in alignment. Data were then taken for wave-length intensity curves. The voltage at which the characteristic radiation first occurs was thus determined and also the positions of the α and β lines. These wave-length-intensity curves were smooth, and there was no suggestion of line radiation other than the α and β. Since this investigation is concerned only with the intensity of the characteristic radiation, no attempt was made to separate the α or the β line into its two components; the intensity of the line in all cases was taken as the maximum of the doublet. For that reason, also, the entire general radiation curve was not taken for each voltage. In order to obtain the intensity of the line radiation, the intensity of the radiation at a point on each side of the line radiation but on the general radiation curve was found; these two points were joined by a straight line, and the distance from this straight line to the peak of the characteristic radiation was taken as the intensity of the characteristic radiation. This process was carried through for each line at each voltage. Observations were made at

intervals of 3 kv up to and including 45 kv. The rate of discharge of the electroscope is a measure of the intensity of the x-rays reaching the ionization chamber, after correction for the natural leak of the instrument. To make this correction, the ionization chamber was rotated several degrees from the correct position at which the particular wave-length would be received in the chamber and the rate of discharge at this point was taken as the natural leak. This varied for different positions of the crystal and of the ionization chamber. It was subtracted from the rate of discharge for a particular wave-length and the result was divided by the electron current passing through the x-ray tube, as measured by a standard calibrated Weston milliammeter. In each case, the intensity recorded is the intensity per unit current through the x-ray tube.

The data for the various intensities for any particular metal were obtained at a single period of operation of the x-ray tube. Necessarily a number of days elapsed during the time of taking the data for all the curves of all the metals. In order to be able to compare the lines from the various metals, the voltage was kept constant; the target was rotated so that each metal in turn sent off x-rays under the same conditions; and the ionization chamber and crystal were rotated into proper positions so that the characteristic α radiation from each metal was in turn reflected into the ionization chamber. In this way data for the α radiation at one voltage from each metal were obtained under as nearly similar conditions as possible. The intensities measured at different times were then multiplied by factors, one for each run, which made the values obtained in different runs such that they could all be compared.

For the purpose of correction for the absorption of the radiation in passing through the mica window of the x-ray tube and also through the mica window of the ionization chamber, a measurement was made of the absorption of each of the characteristic radiations in mica. The absorption coefficients so obtained are given in Table I.

TABLE I

Coefficients of absorption of characteristic radiations from several targets, per cm of thickness

	α line		β line	
	in mica	in metal	in mica	in metal
Silver (47)	5.1	161	3.6	114
Rhodium (45)	7.7	221	5.5	178
Copper (29)	89.2	636	66	470
Chromium (24)	227	867	171	653

The theoretical development by Bergen Davis contains as a constant, the coefficient of absorption of the radiations in the material of the target itself. These coefficients, which are given for the α and β radiations in

Table I, are either taken from the experimental results obtained by Richtmyer (Ag), or were directly determined (Rh), or were estimated from the law of the variation of absorption with atomic number obtained by Richtmyer.

The targets, silver, chromium and rhodium were in the shape of rectangular pieces whose sides varied from 1 to 2 cm in length and whose thickness varied from 1 to 3 mm. The rhodium target was obtained through the kindness of Dr. C. S. Brainin of the Baker Platinum Company. He also furnished the thin sheet of rhodium used in finding the absorption coefficient. This sample of rhodium was exceptionally pure. The targets were held in place by small machine screws.

Calculations, Curves and Results

Corrections. In order to arrive at the actual relative intensities of the radiations as emitted from the target inside the x-ray tube, it was necessary to make the following corrections to the observed data:

(a) For partial absorption in the ionization chamber;

(b) For absorption in the mica window of the ionization chamber and in the mica window of the x-ray tube;

(c) For reflection from the calcite crystal;

(d) For absorption in air path from the crystal to ionization chamber and from the x-ray tube to the crystal.

It has been found by direct observation that the absorption in a column of air saturated with methyl iodide is equal to that of a column of air alone six times its length. Since the length of the ionization chamber of this spectrometer was 150 cm, the equivalent relative absorption and hence ionization was that of an air column 900 cm long. A considerable percentage of the radiation even of shortest wave-length was absorbed in the chamber; hence the corrections were small and a possible error in this method would introduce only a small error in final results.

The mica windows of the ionization chamber and the x-ray tube were respectively 0.001 cm and 0.0014 cm thick. The absorption was calculated and corrected for in the usual manner, using the values of the absorption coefficients given in Table I.

Crystals do not reflect all wave-lengths equally well. Bergen Davis and W. H. Stempel[4] made a careful experimental study of the reflection of x-rays from calcite. One of the crystals which they examined was the one used in this investigation. From their curves it was possible to get directly the reflection for several of the characteristic wave-lengths used. Their experiments did not extend over the entire range of wave-lengths,

[4] Davis and Stempel, Phys. Rev. **17**, 608, 1921

but they found that Darwin's[5] equation agreed very closely with their experimental curve, so this equation was used to extrapolate for values of the reflection beyond the range obtained experimentally. In this way the intensities of radiation for all wave-lengths were corrected for reflection by the crystal.

After all corrections had been made, the resulting intensity was the intensity of radiation leaving the target. These values were plotted

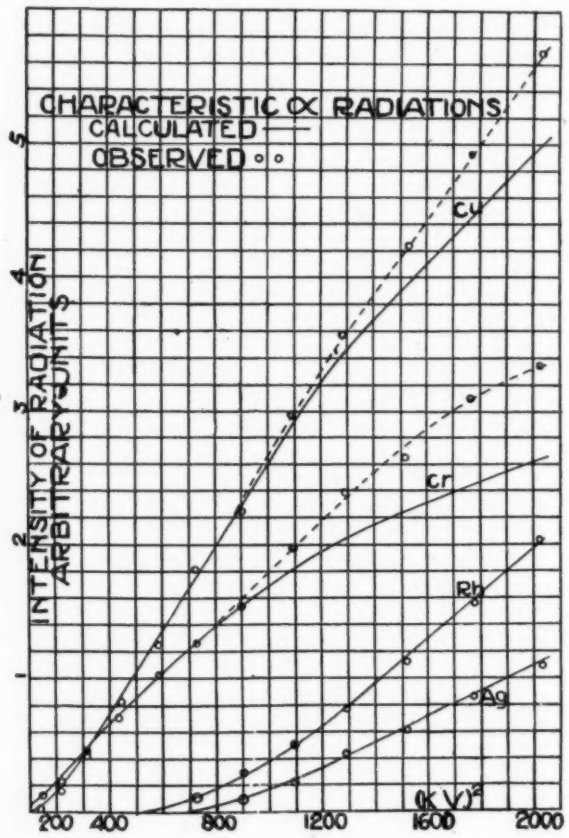

Fig. 1. Intensity of characteristic Kα radiations.

against voltage squared. The resulting curves for metals of higher atomic number were similar in character to those obtained by B. A. Wooten[3] for molybdenum and palladium.

Fig. 1 shows the intensity-voltage curves for the α radiation from all the targets plotted to the same scale. Fig. 2 shows the same for the β

[5] Darwin, Phil. Mag., Feb. and April, 1914

radiation. These curves show that while the characteristic radiation in general increases as the atomic number of the element which is giving off the radiation, decreases, there is an exception to this. The positions of copper and chromium should be reversed.

	Cr	Cu	Rh	Ag
α radiation	2.05	3.1	1.65	0.9
β radiation	0.27	0.5	0.3	0.2

In this investigation several points on the general radiation curve for each voltage were obtained. It was, therefore, possible to compare the intensity of the characteristic radiation with that of the general radiation. In order that the comparison might be of value, this relation was taken at that voltage for each element at which the position of the α line

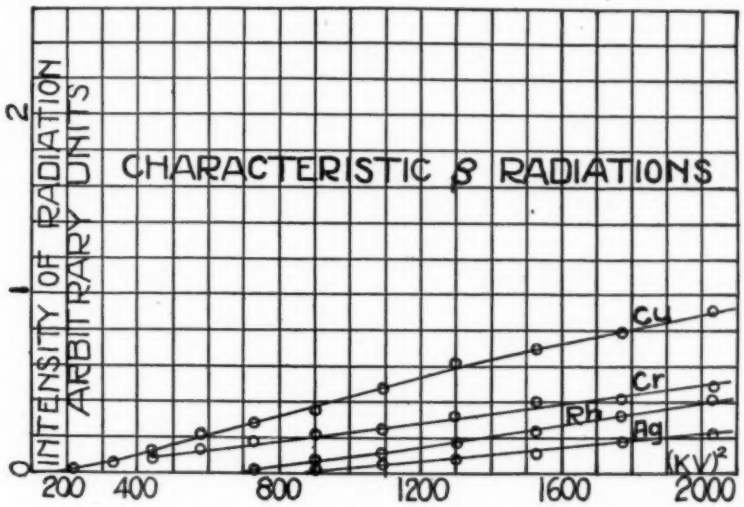

Fig. 2. Intensity of characteristic Kβ radiations.

was on the peak of the general radiation curve. The relation is shown in Fig. 3. The ratio between characteristic and general radiations is small for elements of higher atomic numbers and increases rapidly as the atomic number decreases. The discrepancy in the order of copper and chromium of Figs. 1 and 2 has disappeared in Fig. 3.

These results are in agreement with those obtained by C. S. Brainin.[6] Thus, Figs. 3 and 4 of Brainin's paper show that the total radiation from copper increases decidedly at the voltage at which the characteristic radiation appears, while that from silver decreases at the voltage at which its characteristic is produced. The general radiation obtained from chromium was very small.

[6] Brainin, Phys. Rev. 10, 461, 1917

Comparison with Theory

In the forementioned paper by Bergen Davis,[1] Eq. (5) gives the intensity of the characteristic radiation as a function of the applied voltage. Professor Davis has recently put this equation in a different form, essentially as follows:

$$I=[E_a h n_a B N/b]\ [(1/K^2)\ (1-e^{-K^2(V^2-V_0^2)})-(2V_0/K)e^{-K^2V^2}\int_{KV_0}^{KV}x^2dx]$$

in which for brevity K is put for $\sqrt{(c\mu/b)}$ and the letters refer to the same quantities as in Eq. (5) of that paper. An important property of the

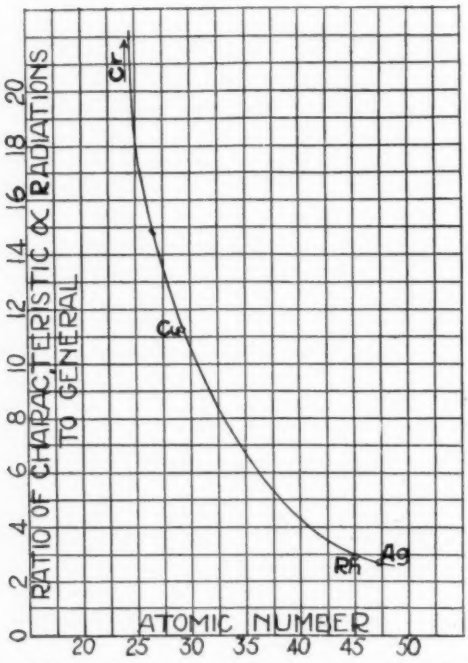

Fig. 3. Ratio of $K\alpha$ radiations to general as a function of atomic number.

above equation is that it contains no arbitrary constants. The constants b, c, and μ (hence K) are obtained from data already published or obtained in this investigation. The constant b is the constant a of Whiddington's[7] equation,

$$v_x^4=v^4-ax$$

when referred to voltages instead of velocities. Actual measurements were made by Whiddington only on aluminum and gold. His results show that $a/\rho^{0.6}$ equals a constant approximately, where ρ is the density. This relation was used in calculating b for the elements of the present

[7] Whiddington, Pro. Roy. Soc. **86**, 1912

investigation. The constant c is the ratio of the length of path of the rays in emerging from the target, to the depth of penetration of the electron producing them, and was equal to 2.07. The constant μ is the coefficient of absorption given in Table 1. Using these constants, the variable part of the equation was calculated to give the shape of the curve. The observed and calculated curves were then made to agree at one point. The extent of the agreement is shown by Fig. 2. The calculated values are shown by the solid line, while the points plotted are the observed values. There is good agreement between calculated and observed curves for elements of higher atomic number, but the agreement is not so good for elements of lower atomic number. It was suggested that the increased

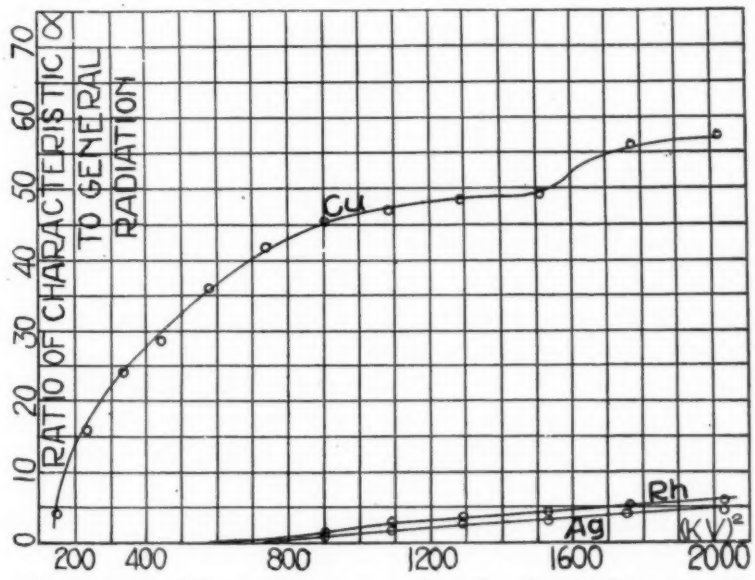

Fig. 4. Ratio of Kα radiations to general as a function of voltage squared.

radiation from the elements of lower atomic number might be due to the higher order of spectra of shorter wave-length. This is probably not the case, for the general radiation would then have contained the same increase from the higher order of spectra of shorter wave-lengths. On the other hand these curves suggest that these metals are fluorescent and that the increased radiation is due to that cause.

The theory fails to take into account the fluorescent production of characteristic radiation by the absorption of the general radiation. Yet this absorption and fluorescent re-emission of characteristic radiation is probably of considerable importance in case of the elements of lower atomic numbers.

Too much importance should not be attached to the extent of the above agreement with theory for the following reasons:

(a) The uncertainty as to the accuracy of the corrections to the observations to give the true form of energy of emission from the target;

(b) The uncertainty as to the law of decrease of electronic velocities in penetrating the target, and also the uncertainty as to the value of the constant b, in case Whiddington's law is correct.

In the equation, the constant $E_\alpha h n_\alpha$ may be interpreted as expressing the particular characteristic radiation from the atom itself. Since the constant BN/b is the same for any one element, the ratio $E_\alpha h n_\alpha / E_\beta h n_\beta$ expresses the theoretical ratio of intensities of the α and β radiations as emitted from the atom. The observed ratio I_α / I_β, the corrected ratio, and the ratio of atomic emissions are given in Table II.

TABLE II

Target	Observed ratio	Corrected ratio	Atomic emission ratio
Silver (47)	6.00	4.65	4.83
Rhodium (45)	5.68	4.75	5.96
Copper (29)	4.7	6.53	7.33
Chromium (24)	3.2	7.36	12.35

In Fig. 4 the curves showing the relation between the ratio of the characteristic α radiation to the general and the voltage squared are drawn. The curve for chromium is not shown because the values for the general radiations were very small. The relation is a straight line function for silver and rhodium but copper shows quite a variation. Apparently no general law of variation for the slopes of these curves exists.

In conclusion, I wish to express my sincere thanks to Prof. Bergen Davis, who suggested the work, and whose interest and enthusiasm have been a source of inspiration to me in this and in other work. I am grateful also to Dr. C. S. Brainin for the help in securing the rhodium sample.

PHOENIX PHYSICAL LABORATORY,
COLUMBIA UNIVERSITY,
June 19, 1923.

THE ABSORPTION OF X-RAYS BY IRON, COBALT, NICKEL AND COPPER[1]

BY F. K. RICHTMYER AND F. W. WARBURTON

ABSTRACT

X-ray absorption coefficients of Fe, Co, Ni and Cu, for wave-lengths below the K absorption limit, have been measured by the use of a large spectrometer with a selected calcite crystal giving a beam of exceptional purity. The chief difficulty was to secure uniform films of the pure metals. It is found that the sequence of values of the atomic coefficients is that of the atomic numbers, not that of atomic weights, and that the *variation with atomic numbers* is as the fourth power, as previously suggested, the relation $\mu_a = 22.4 \times 10^{-27} N^4 \lambda^3 + \sigma_a$, holding within experimental error for all the ten elements for which the results have been obtained, from $N = 6$(C) to $N = 82$(Pb), except possibly iron for which the experimental value is 3 per cent too low. The values for *carbon, lead and tungsten* are preliminary and are taken from data not yet published.

Method of producing a thin uniform sheet of cobalt suggested by Kayko. Chemically pure oxide was compressed to a thin placque, then reduced in a furnace by an atmosphere of hydrogen.

SINCE the work of Moseley the significance of atomic number, as distinguished from atomic weight, in connection with a number of the properties of the elements, has come to be very fundamental. But most of these properties have to do with frequency phenomena rather than with energy relations. Thus in the case of cobalt and nickel, in which the orders of atomic numbers and of atomic weights are inverted, Duane and Hu have shown[2] that the frequencies of the K absorption limits of the two elements are in the same order as the atomic numbers.

It is to be expected that where energy relations, as distinct from frequencies, are involved, the atomic number, rather than atomic weight, of the element would also be fundamental. And Duane has shown[3] that the intensity of the general radiation from the elements Fe, Co, Ni and Cu follows the sequence of atomic numbers, not that of atomic weights. Further Owen,[4] Richtmyer,[5] and others have shown that the

[1] Grateful acknowledgment is made for a grant from the Heckscher Research Council of Cornell University to F. K. Richtmyer. Without this grant this work would have been quite impossible.

[2] Duane and Hu, Phys. Rev. **14**, 516 (1919)

[3] Duane, Phys. Rev. **11**, 491 (1918)

[4] Owen, Proc. Roy. Soc. **94**, 510 (1919)

[5] Richtmyer, Phys. Rev. **18**, 13 (1921)

atomic absorption coefficient of x-rays is a simple function of the fourth power of the atomic number.

The atomic absorption coefficient is defined in the following way. Numerous researches have shown that for any given substance for wavelengths less than the K absorption limit the mass absorption coefficient μ/ρ is given by the empirical equation

$$\mu/\rho = F\lambda^3 + \sigma/\rho \tag{1}$$

where μ is the exponent in the ordinary absorption law $I = I_0 e^{-\mu x}$, ρ is the density of the material, σ/ρ is a constant which is frequently identified with the scattering, and F is a constant (very nearly). By dividing both sides of this equation by the number of atoms per gram, equal to n/A where n is Avogadro's constant and A the atomic weight, one obtains

$$\frac{\mu}{\rho}\ \frac{A}{n} = \mu_a = F\ \frac{A}{n}\ \lambda^3 + \frac{A}{n}\ \frac{\sigma}{\rho} = F_a\lambda^3 + \sigma_a \tag{2}$$

where μ_a is the atomic absorption coefficient and F_a and σ_a are constants.

In the previous experiments above referred to,[5] a curve plotted between log F_a and log N, where N is the atomic number, for the four elements Al, Cu, Mo and Ag gave a straight line with a slope 4.00; i.e.

$$F_a = kN^4 \tag{3}$$

If, however, a curve be plotted with log F_a and log A as coordinates, a straight line nearly as good results, with a slope 3.7. So that one might write

$$F_a = kA^{3.7} \tag{4}$$

It is of importance to decide whether (3) or (4) is correct. A determination of the value of F_a for the series of elements Fe, Co, Ni and Cu should answer the question since the order of atomic number and of atomic weight in Co and Ni is inverted.

Apparatus and Method

The absorption measurements were made by use of an x-ray spectrometer of the Bragg type specially constructed[6] in the instrument shop of the Department. Since instruments of this type are so well known, no description need be given, excepting as regards a few minor points. The x-ray beam was limited by two bilaterally and independently adjustable micrometer slits, 2.5 cm long, and 37 cm apart placed *between* the crystal and the x-ray tube. These slits were, for most of the measurements, kept at widths between .015 cm and .025 cm, thus giving a very

[6] The writers' thanks are due to Mr. F. E. Miller, whose skill as an instrument maker and ingenuity as a designer made possible the spectrometer by which these measurements were made.

narrow beam. The crystal was the split (and not polished) calcite crystal No. A_3 described by Bergen Davis[7] and used by him in his measurements on the monochromaticity of beams reflected by various crystals. This particular crystal when used with the very narrow slit system above mentioned gave a beam of exceptional purity. The ionization chamber was of the usual type, filled with methyl bromide, the ionization currents being measured by the rate of drift of a Compton electrometer, reconstructed in the Department shop, and operated at a sensitivity of approximately 1500 mm per volt.

The x-ray tube[8] was a tungsten target tube, of the radiation type, capable of operating at 200,000 volts (peak). Special attention was paid to keeping the voltage applied to the tube and the current through it constant. Neither varied by as much as $\frac{1}{2}$ per cent during a run.

The leakage current through the ionization chamber was almost entirely compensated by connecting an opposing voltage, the best value of which was determined by trial, to the metal tube forming part of the electrostatic screening of the wire connecting the rod of the ionization chamber to the electrometer. Correction was made for any residual drift.

In making precision measurements of x-ray absorption coefficients, not so much difficulty is experienced in making the x-ray measurements as in getting chemically pure materials sufficiently homogeneous and of uniform thickness. The matter of purity is particularly important in measuring the absorption coefficients of the light elements. Consider, for example, carbon, with iron as an impurity. At $\lambda = .5$ A the mass absorption coefficient of carbon is approximately .30; that of iron approximately 15.0. The mass absorption coefficient of carbon containing 0.1 per cent of iron would differ from that of *pure* carbon by 4.5 per cent. At $\lambda = 1.0$ A the error would be 6.5 per cent. However, an impurity of low atomic number in a substance of high atomic number will cause no greater proportionate error than is made in getting the density of the sample. Thus the absorption coefficient of iron containing 0.1 per cent of carbon would differ from that of pure iron by only about 0.1 per cent.

Homogeneity and uniformity of thickness are, in some substances, very difficult to secure, particularly in elements of high atomic number, where one must work with samples only a fraction of a mil thick. Even

[7] Davis, Phys. Rev. **17**, 608 (1921). The crystal was kindly loaned to one of the writers (F. K. R.) by Dr. Davis.

[8] For this tube the writers are indebted to Dr. W. D. Coolidge of the General Electric Co. Also the 150,000 volt 10 kv-a transformer used with the tube, was loaned by the General Electric Co.

though one can secure the pure material in this thin form, one must measure its thickness to, say, one-half per cent, or determine the mass per square centimeter with that precision. The *average* mass per square centimeter can readily be obtained by weighing a strip of the material of known area, but this does not necessarily give the mass per square centimeter at *every* point unless the specimen be of uniform thickness.

The iron used in the present investigation was electrolytic iron obtained from the General Electric Company. The nickel and the copper were obtained from Eimer and Amend. Much difficulty was experienced in obtaining the cobalt in the form of a thin strip. The pure metal could be obtained from several sources but it could not be worked. Electroplating cobalt onto aluminum, and stripping off the cobalt layer was tried, but without success. The writers are indebted to Mr. C. J. Kayko for the final solution of the problem. Working at the General Electric Research Laboratory, in Schenectady, he took chemically pure cobalt oxide, bolted it twice through fine silk, and then under a pressure of several tons per square inch pressed it into a thin placque. This was then placed in a furnace in an atmosphere of hydrogen until the oxide was reduced to metallic cobalt. A fine, firm adherent strip of exceptionally uniform composition and thickness was obtained.

Since, for any given substance, the mass absorption coefficient is very

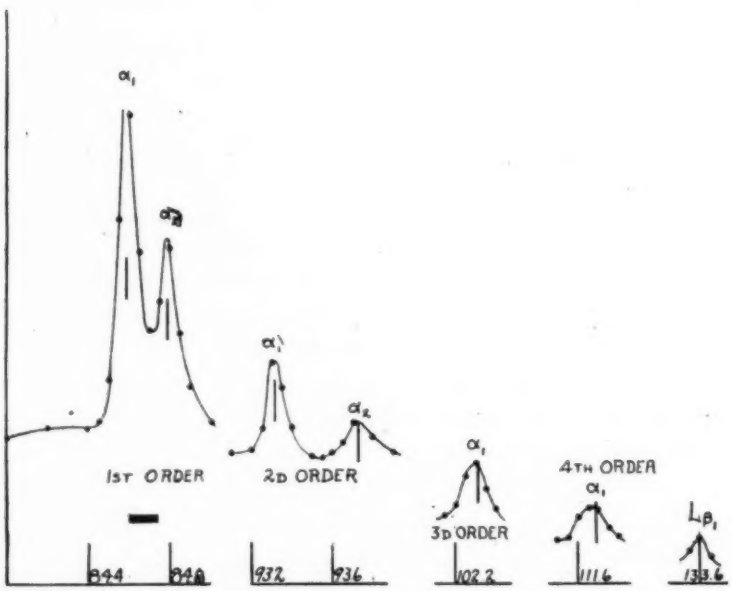

Fig. 1. Calibration of spectrometer.

nearly a linear function of the cube of the wave-length, it is important in determining the value of F in equation (1) that the wave-length measurements be made with as high precision as possible. A calibration curve was computed for the various chamber angles of the spectrometer by means of the known grating space of calcite. This curve was checked by the several orders (first to fourth) of the α lines of tungsten. The check is shown graphically in Fig. 1. The abscissas are sections of the spectrometer scale (arbitrary units). The short vertical lines show, for the several orders, the computed position of the lines, and the full lines indicate the observed position. The agreement is seen to be excellent. The graph also shows the high resolving power of the apparatus, the lines α_1 and α_2, which differ by about .004 A, being well separated in the first order spectrum. The equivalent "slit width" is shown by the small rectangle under the first order, and, at the first order of the α lines ($\lambda = .211$ A) is about .0028 A.

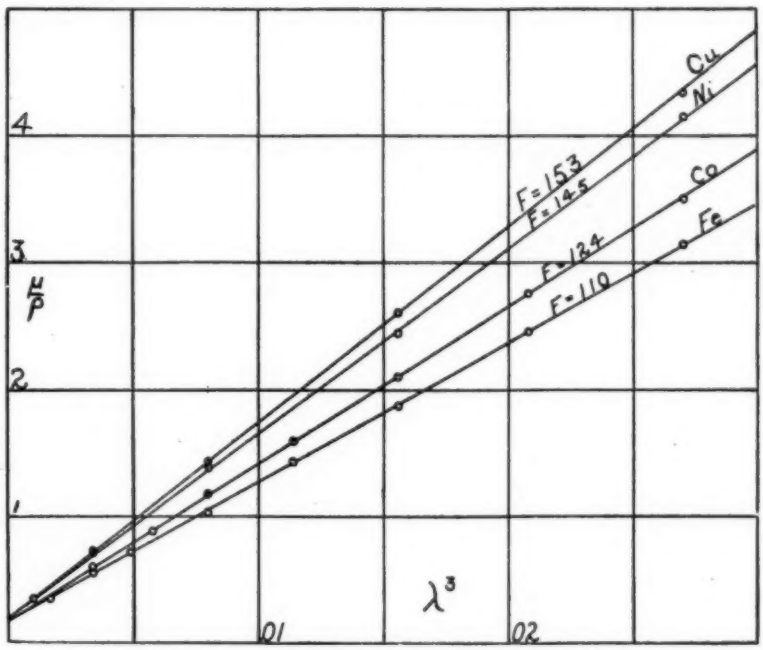

Fig. 2. μ/ρ as a function of λ^3 for Fe, Co, Ni and Cu.

RESULTS

The mass absorption coefficients as a function of the cube of the wave-length, for Fe, Co, Ni and Cu, are shown graphically in Fig. 2 for the wave-length range $.12 \text{ A} < \lambda < .30 \text{ A}$. Over this range the following equations hold.

$$\text{For Fe } \mu/\rho = 110\lambda^3 + .18$$
$$\text{Co } \mu/\rho = 124\lambda^3 + .18$$
$$\text{Ni } \mu/\rho = 145\lambda^3 + .20$$
$$\text{Cu } \mu/\rho = 153\lambda^3 + .20$$

Wave-length is expressed in angstrom units. If now these several values of F be divided by n/A one obtains F_a in column four of the following table.

Element	N	F	F_a	$\log_{10} F_a$	$\log_{10} N$
Fe	26	110	101×10^{-23}	-20.006	1.415
Co	27	124	121	.081	1.431
Ni	28	145	140	.148	1.447
Cu	29	153	161	.206	1.462

The relation between log F_a and log N is shown graphically in Fig. 3. The line is drawn to a slope of 4.00. All points fall on this curve within experimental error with the possible exception of that for iron, for which the mass absorption coefficient would have to be increased by about 3 per

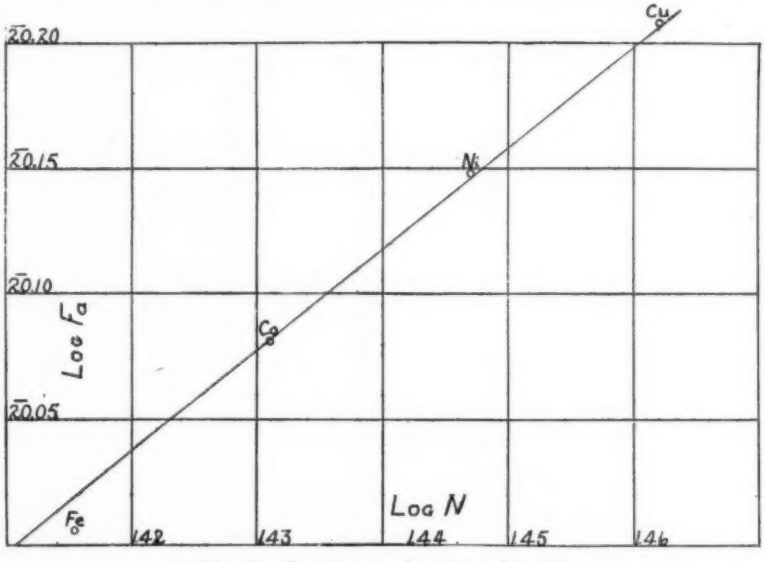

Fig. 3. Log F_a as a function of log N.

cent. Whether this difference for iron is real or is the result of some as yet undetected experimental error remains to be determined. The agreement in the case of cobalt and nickel is so excellent as to leave no room for doubt as to the correctness of Eq. (3) as contrasted with (4).

To bring out more clearly the correctness of Eq. (3) there is collected in graphical form in Fig. 4 the results recorded in this paper for Fe, Co, Ni and Cu and also some previous data.[5] This curve, like Fig. 3, is drawn to a slope of 4.00. The values for carbon, lead and tungsten are from unpublished data. That for carbon has been corrected for a slight

impurity; that for tungsten as well as for lead is somewhat in doubt because of the difficulty of getting the material in thin enough strips. On the basis of this curve one may make a slight correction to the empirical equation for atomic absorption coefficients previously given,[9] viz.

$$\mu_a = 22.4 \times 10^{-27} N^4 \lambda^3 + \sigma_a$$

The numerical factor previously given was 22.9×10^{-27}.

It should be borne in mind that this equation holds only for wave-lengths considerably below the K absorption limit, since further and more careful observations have confirmed the previous conclusion that

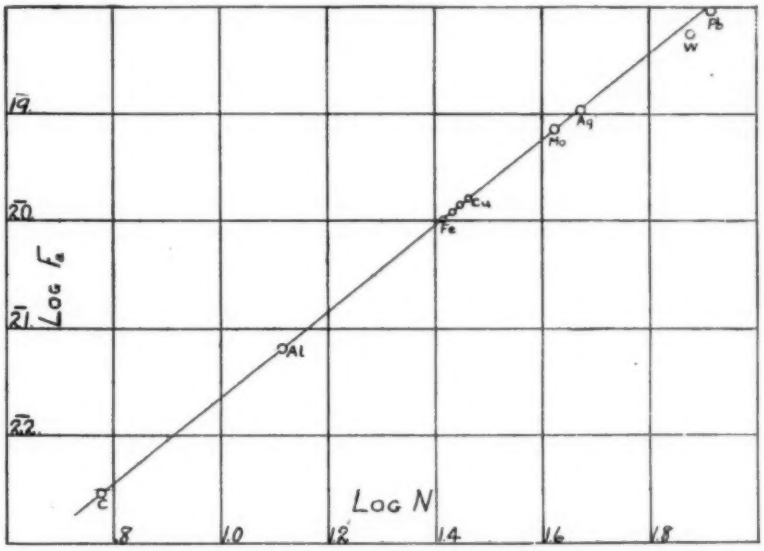

Fig. 4. Log F_a as a function of log N.

there is a real departure from the λ^3 law in the neighborhood of the K limit. The *exact* value of F and of F_a will therefore depend somewhat on the wave-length range used. This may in part explain the low values for tungsten and for lead.

On the basis of present data it seems unlikely that there is any periodicity in the values of F_a in the atomic number series, but the number of elements for which careful measurements are available is insufficient to decide the question beyond doubt. Work is in progress to test this point and to ascertain the change in F_a on passing the K limit, as a function of atomic number.

CORNELL UNIVERSITY,
June 16, 1923.

[9] Loc. cit.[5] Eqs. 6 and 6′ in this former paper unfortunately contain as an error a factor 10.

NOTE ON RELATIVISTIC RÖNTGEN L-DOUBLETS AND THE SCREENING CONSTANT; A CORRECTION

By J. B. Green

Abstract

A more accurate method of computing the screening constant shows that the previous conclusion is incorrect, and that the screening constant would not be constant if terms beyond the third were neglected in accordance with Bohr's suggestion.

In a recent paper with the above title[1] there is a discrepancy which has just been called to my attention. In that paper, if expression (e) is identical with the first three terms of the expansion of (b), the value of s deduced therefrom should be smaller than the value of s deduced from (b) since all the terms in the expression are positive. This, however, does not turn out to be the case, the values of s from (e) in every case coming out larger than the values from (b). The reason for this discrepancy is that in the course of the derivation of (e) from (d), using the first three terms of the binomial expansion of (b), some uncompensated error was introduced. For, if we expand (e) in power of $(Z-s)^2$ the result is, writing φ for $\frac{1}{4}\alpha^2(Z-s)^2$,

$$\Delta\nu/R=\varphi^2\left\{1+\tfrac{5}{2}\varphi+\tfrac{5}{8}\tfrac{3}{}\varphi^2+\tfrac{1}{6}\tfrac{2}{4}\tfrac{7}{}\tfrac{5}{}\varphi^3+\cdots\right\}$$

differing from (d) after the third term in the expansion. For a given $\Delta\nu/R$, then, we see that the value of s will be larger if calculated from (e) than those from (b). If we calculate s by trial and error from the first three terms of (d) we find the values 3.321 and 3.030 for Z equal to 81 and 90 respectively. These values depend more on Z than those calculated from the complete formula (b), a result which would seem to reverse the conclusions set down in my previous paper.

My thanks are due to Professor Sommerfeld for calling my attention to this discrepancy, which was noticed by one of his students.

University of Wisconsin,
August 10, 1923.

[1] Green, Phys. Rev. **21**, 397, April, 1923

TWO NOTES ON QUANTUM CONDITIONS

By J. H. Van Vleck

Abstract

Selection of coordinates for use in evaluating the Sommerfield quantum integrals.—It is well known that these coordinates need not necessarily satisfy Lagrange's equations, and a general criterion for the choice of such variables is given in the present paper, in which it is shown that all sets of p's and q's which (a) satisfy Hamilton's equations, (b) separate the variables, and (c) are of such a character that the average value of the kinetic energy is equal to that of $\frac{1}{2}\Sigma_1^n p_i\dot{q}_i$, will give the correct energy levels when employed in the quantum integrals $\int p_i dq_i = n_i h$; $(i = 1, 2, \ldots\ldots, n)$. This general class of coordinate systems includes as special cases the familiar normalized Schwarzschild angle variables and Lagrangian generalized coördinates which separate the variables.

Combination of Hamilton's principle with Trkal's method for quantizing conditionally periodic systems is proposed which, like Hamilton's principle, determines the character of the motion permitted by the Newtonian dynamics, and in addition quantizes the orbits by specializing the constants of integration in accordance with the conventional quantum conditions. This variation principle includes formally in a single equation the results of classical dynamics and the Sommerfield quantum conditions, which together determine the sizes and shapes of electronic orbits. The principle is illustrated by an application to a non-linear oscillator in which the potential involves the second and fourth powers of the displacement from the equilibrium position.

PART I

The Choice of Coordinates in the Evaluation of Quantum Integrals

LET us consider a dynamical system of n degrees of freedom with kinetic energy T and potential energy V. The Sommerfeld-Wilson quantum conditions require that

$$\int p_i dq_i = n_i h \qquad (i = 1, 2, \ldots n)^1 \tag{1}$$

where $n_1, n_2, \ldots, n_n$ are integers and each integration is to be extended over a complete cycle of values for q_i. It is usually stated that the q_i are a set of "generalized coordinates" satisfying the Lagrangian equations

$$\text{I} \qquad \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_i}\right) - \frac{\partial L}{\partial q_i} = 0 \qquad \text{where } L = T - V$$

while $p_1, p_2, \ldots, p_n$ are the corresponding momenta defined by the relations

[1] Throughout the article it is to be understood that the subscript i ranges from 1 to n, where n is the number of degrees of freedom.

II $$p_i=\frac{\partial T}{\partial \dot{q}_i}.$$

In consequence of I and II it can be proved that the p_i and q_i satisfy the Hamiltonian canonical equations, so that we may write

III $$\frac{dq_i}{dt}=\frac{\partial H}{\partial p_i}, \quad \frac{dp_i}{dt}=-\frac{\partial H}{\partial q_i}$$

where H is the Hamiltonian function, or energy.

In evaluating the quantum integrals given in (1) the choice of an appropriate set of generalized coordinates is of fundamental importance. It is essential that the integrand p_i be expressible as a function of only the variable of integration q_i, rather than of all n coordinates, so that we have

IV $$p_i=f(q_i)$$

Unless the above condition is satisfied, it is usually impossible to determine the cycle over which the integration is to be extended, and the quantum integrals then lose all meaning.[2]

Unfortunately in many problems, coordinates which conform to all the requirements of the preceding paragraph cannot be found. To escape from this difficulty, coordinates must be employed which satisfy conditions III and IV, but not necessarily I and II. Coordinates for which III is valid are usually termed "canonical" and include as a special case ordinary "Lagrangian" or "positional" coordinates satisfying I and II in addition to III.[3]

[2] The requirement IV can be proved equivalent to the demand that a set of coordinates be found which "separate the variables" in the Hamilton-Jacobi partial differential equation.

[3] The simplest and most frequently encountered type of coordinates possessing the properties III and IV but not I and II are the so-called "Schwarzschild angle-variables" ("Winkelkoordinaten"), which we shall denote by $Q_1, Q_2, \ldots, Q_n, P_1, P_2, \ldots P_n$. In conditionally periodic dynamical systems, solutions of the equations of motion may be described by multiple Fourier series of the form

$$x_i=\Sigma\Big\{A(\tau_1,\tau_2,\ldots,\tau_n)\cos[2\pi(\tau_1\nu_1+\tau_2\nu_2+\ \ldots\ +\tau_n\nu_n)t] + B(\tau_1,\tau_2,\ldots,\tau_n)\sin[2\pi(\tau_1\nu_1+\tau_2\nu_2+\ \ldots\ +\tau_n\nu_n)t]\Big\}$$

where the x_i are Cartesian coordinates fixing the positions of the particles or electrons, and the summation is to be extended over all positive and negative integral values of the numbers $\tau_1,\tau_2, \ldots, \tau_n$. In such systems it is possible to find a particular set of canonical coordinates $Q_1, Q_2, \ldots, Q_n P_1, P_2, \ldots, P_n$ such that the P_i are constants, independent of the time, while the Q_i satisfy the relations $Q_i=\nu_i t+\epsilon_i$ (the ϵ_i being constants), and hence are linear functions of the time such that an alteration of any one of them by unity (the other Q_i remaining fixed) leaves the configuration of the dynamical system unaltered. Because of these characteristic properties the Schwarzschild angle-variables must be regarded as intrinsic coordinates of fundamental importance.

It is of interest to examine whether the Sommerfeld quantum integrals can be expressed in terms of any set of coordinates which satisfy equations III and IV (i.e. any system of canonical coordinates which "separate the variables"). These two conditions do not appear to impose sufficient restrictions to yield a consistant theory of quantum conditions. In the case, for instance, of an electron rotating with an angular velocity $d\varphi/dt$ in a relativistic hydrogen atom, the conditions III and IV will be satisfied if in setting $\int_0^{2\pi} p_\varphi d\varphi = nh$ we take p_φ equal to the angular momentum of the electron plus any multiple of e^2/c, a quantity which has the dimensions of angular momentum. The correct energy will not be obtained if the additive multiple of e^2/c is different from zero. Difficulties of this nature, however, can be avoided if in addition to III and IV we impose the restriction that the coordinates in the quantum integrals be of such a type that

V $$\overline{T} = \tfrac{1}{2}\Sigma_1^n \overline{p_i \, dq_i/dt}$$

where the bars denote average values.[4] This interpretation of the bars is to be understood throughout the article. It will be proved that all sets of p's and q's satisfying III, IV, and V will yield identical values for the energy when employed in the quantum integrals, and consequently the quantum conditions given in Eq. (1) can be applied with validity to all such coordinate systems.[5] The exact nature of the restriction V as

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The preceding requirements do not determine the P_i uniquely, and to remove this ambiguity it appears necessary, as shown by Burgers (Versl. Akad. Amsterdam, **25,** 1055) to add the restriction that these quantities be defined in such a way as to make valid the Ehrenfest adiabatic hypothesis. Burgers has proved that this demands that the expression

$$W = 2\int_{t_0}^{t} T dt - \Sigma_1^n [P_i Q_i]_{t_0}^{t}$$

be periodic in each of the Q_i when considered as a function of the Q_i and P_i. We shall term as "normalized" any set of angle variables which conforms to this requirement. It follows immediately from the above limitation on W that all normalized angle variables conform to the condition V of the present article. Conditions III and IV are satisfied even without this normalization, for the P_i and Q_i are by definition mutually conjugate (i.e. satisfy III), while the P_i, being constant with respect to the time, are independent of all the Q_i and hence comply with IV.

[4] In many problems it can be shown from dimensional considerations that an equation of the form V must be satisfied if the p_i and q_i are to have any physical meaning (i.e., the proper dimensional properties). In the case, for instance, of a hydrogen atom governed by Newtonian mechanics, a mutiple of e^2/c cannot be added to the angular momentum in defining p_φ because the velocity of light does not appear in the equations of motion.

[5] It should, however, be mentioned that whereas all sets of p's and q's satisfying III, IV, and V will give the correct energy value when employed in the quantum integrals, all such coördinate systems will not necessarily give the proper form for the orbits in certain exceptional types of dynamical systems (viz., "degenerate" systems, in which the number of degrees of freedom exceeds the number of intrinsic frequencies; also systems in which for all values of the constants of integration the vibration frequencies

applied to coordinates other than angle variables, and the great generality of the coordinates which can be used in the quantum integrals even after this limitation is imposed, do not appear to be clearly emphasized in the literature of the quantum theory, although this information can perhaps be implied from discussions given by Burgers[6] and Epstein.[7] Normalized angle variables, used by Schwarzschild and others, and Lagrangian generalized coordinates[8] which "separate the variables" must be regarded as by far the most important special cases of the general type of coordinates specified by III, IV, and V.[9]

Proof of Sufficiency of Conditions III, IV, and V. The statement made in the preceding paragraph that all sets of coordinates satisfying III, IV, and V will yield the same values for the energy when employed in the quantum integrals is perhaps most readily established by comparing the Sommerfeld quantum conditions with a very ingenious method of quantization devised by Trkal which is independent of the coordinate system.[10] Trkal's theory demands that the constants of integration be so chosen that when they are varied from the correct quantized values the relation

$$\delta F = 0 \tag{2}$$

is satisfied, where

$$F = [\overline{T} - \overline{V} - \Sigma_1^n n_i h\nu_i] \tag{3}$$

In Eq. (3) $\overline{T}$ and $\overline{V}$ denote the average kinetic and potential energies respectively while the ν's are the intrinsic vibration frequencies of the

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satisfy any relation of the form $\Sigma c_i\nu_i = 0$, where the c_i are fixed constants independent of the initial conditions.) In degenerate systems the quantum theory does not demand that the shape of the orbit be uniquely determined, while the second exceptional case cited in the preceding sentence appears to be of purely academic interest.

It is tacitly assumed in the present article that each coordinate q_i either undergoes periodic oscillations or else is of the "cyclic type" so that the configuration of the system is periodic in this coordinate; otherwise the limits of integration in I have in general no meaning.

[6] J. M. Burgers, Versl. Akad. Amsterdam, **25**, 1055, 1917

[7] P. Epstein. Ann. der Phys. **51**, 168

[8] The relation V is satisfied by any system of Lagrangian coordinates, even when the average value signs are removed. This is easily proved by applying Euler's theorem on homogeneous quadratic functions to the kinetic energy and then using II. (Cf., Sommerfeld, "Atombau," 3rd ed., p. 658.)

[9] If relativistic rather than Newtonian dynamics are to be employed, equations III, IV and V are still the fundamental conditions governing the choice of coordinates for the quantum integrals, but in V the kinetic energy must be replaced by the function $\psi = \frac{1}{2}\Sigma m_k v_k^2 \sqrt{(1 - v_k^2/c^2)^{-1}}$ where v_k and m_k are the velocity and rest mass of the kth particle (electron or nucleus) and the summation is to be extended over all the particles in the system.

[10] V. Trkal, Cambridge Phil. Soc., Proc. **21**, pp. 80-90, May, 1922.

system.[11] Trkal has proved that the Sommerfeld quantum conditions (1) require that (2) be satisfied, provided the integrals in (1) be evaluated in terms of Lagrangian generalized coordinates, which satisfy I and II in addition to III, IV, and V. Although Trkal's proof apparently assumes that $T=\frac{1}{2}\Sigma_1^n\ p_i\dot{q}_i$, a relation which is only true in general for Lagrangian coordinates, no essential modification is required if we assume that this equation holds true only on the average, so that it becomes identical with our condition V. The other steps in Trkal's proof do not require alteration if a set of p's and q's satisfying only III, IV, and V be employed in the Sommerfeld quantum integrals, and consequently, even when expressed in terms of such coordinates, the quantum conditions (1) require that (2) be satisfied. Since (2) in general determines the energy uniquely, all sets of coordinates satisfying III, IV, and V will therefore give a common quantized value for the energy. To establish the correctness of this common value, it suffices to show that one particular set of such variables can validly be used in the quantum integrals. It is generally conceded that the Sommerfeld quantum conditions can be applied to the following special coordinate systems belonging to the general class satisfying III, IV, and V:

(a) a set of Lagrangian generalized coordinates which separate the variables

(b) a set of Schwarzschild angle variables P_i and Q_i in which the P_i have after the method of Burgers been normalized in accordance with the Ehrenfest adiabatic hypothesis.

Neither coordinates of type (a) or (b) exist for all dynamical systems. However, it is well known that variables of the latter class are much more general than those of the former and can be found for all conditionally periodic systems. We may therefore conclude that in such systems all sets of coordinates satisfying III, IV, and V will give a correct common value for the energy when employed in the quantum integrals.

It follows as an interesting corollary of the proof given in the preceding paragraphs, that Trkal's quantum conditions are identical with those of Sommerfeld even when the quantum integrals of the latter are formulated in terms of the very general type of coordinates satisfying only III, IV and V. Trkal's method can therefore be employed in any dynamical system for which a solution of the equations of motion can be represented by means of multiple Fourier series, even though the quantum integrals must be evaluated in terms of angle variables because a separation of variables cannot be effected with ordinary Lagrangian coordinates.

[11] In some exceptional cases (2) does not determine the energy uniquely, and it is then necessary to add the restriction that the average value of $T=\frac{1}{2}\Sigma_1^n n_i h\nu_i$. This relation is usually satisfied in virtue of (2).

PART II

AN EXTENSION OF TRKAL'S VARIATION PRINCIPLE

Let us now consider a dynamical system specified by n generalized coordinates $q_1, q_2, \ldots, q_n$. We shall assume that the q's can be developed as multiple Fourier series for all values of the time, so that we may write

$$q_i=\Sigma\{A^i(\tau_1, \tau_2, \ldots, \tau_n)\cos[2\pi(\tau_1\nu_1+\tau_2\nu_2+\ldots\tau_n\nu_n)t] +B^i(\tau_1, \tau_2, \ldots, \tau_n)\sin[2\pi(\tau_1\nu_1+\tau_2\nu_2+\ldots\tau_n\nu_n)t]\} \quad (4)$$

where the summation is to be extended over all positive and negative integral values of $\tau_1, \tau_2, \ldots, \tau_n$. According to the classical dynamics the amplitudes A and B,[12] together with the vibration frequencies ν_i, must be determined as functions of $2n$ arbitrary constants of integration by solving the Lagrangian equations of motion I. Let these amplitudes and frequencies be varied in such a way that the q's always satisfy the Lagrangian equations. This can be done by expressing the A's, B's and ν's in terms of the constants of integration and then altering the values of the latter. Then according to Trkal's quantum conditions, out of the totality of orbits satisfying the Lagrangian equations, which are generated by the above variation process, the particular orbit appropriate to the quantum numbers $n_1, n_2, \ldots, n_n$ is determined by the relation

$$\delta F=0 \quad \begin{array}{l}\text{(amplitudes and frequencies being varied}\\ \text{in accordance with classical dynamics by}\\ \text{altering the constants of integration)}\end{array} \quad (5)$$

where δF denotes the first variation of the function F defined in Eq. (3). Throughout the present discussion F is to be regarded as a function of the A's, B's, and ν's, as these quantities are involved implicitly through the q's, which enter into the formulas for T and V, and which are to be expressed by series of the form (4).

Although Trkal requires that the variational orbits conform to the classical dynamics, this restriction does not appear necessary. Let us instead remove the limitation that the q's satisfy the Lagrangian equations throughout the process of variation, and admit any set of q's which can be represented by series of the form (4), so that in the variation the A's, B's, and ν's are no longer restricted to be functions of $2n$ arbitrary constants, but may all be assigned perfectly arbitrary values (subject to the limitation that the change in the q's be small). It is the purpose of

[12] We shall for simplicity in general write A in place of $A^i(\tau_1,\tau_2, \ldots \tau_n)$, with a similar abbreviation for the B's. It is to be understood, however, that an expression of the form A involves the arguments i and $\tau_1,\tau_2, \ldots, \tau_n$.

the present article to show that then the equation

$$\delta F = 0 \qquad \text{(amplitudes and frequencies being varied arbitrarily, without regard to dynamics)} \qquad (6)$$

automatically specializes the amplitudes and frequencies in such a way as to make the q's conform to the Newtonian mechanics. This rule, which we shall refer to as "the extended Trkal variation principle," closely resembles Hamilton's principle, for both employ non-dynamical variational orbits and enable one to determine the particular orbits which comply with classical dynamics; (the former, however, has the additional restriction that the variational orbit be capable of representation by a multiple Fourier series). Because of this similarity, the condition (6) may, like Hamilton's principle, be regarded as a substitute for the Newtonian or Lagrangian equations of motion. In addition (6) determines the constants of integration in accordance with the conventional quantum conditions. In a conditionally periodic system this single equation therefore combines all the requirements of the classical dynamics and the Sommerfeld quantum conditions, which together determine the sizes and shapes of electronic orbits. Thus out of all motions which can be described by multiple Fourier series, the actual orbit alone is characterized by the validity of (6).

Proof of the extended Trkal variation principle. The first step in establishing the extended variation principle consists in showing that if the ν's are held fast but the infinite set of A's and B's is varied in any manner subject to the restriction that the alteration in the q_i be small, then the classical dynamics requires that

$$\delta F = 0 \qquad \text{(amplitudes varied, frequencies held fast)} \qquad (7)$$

The usual method of computing the variation of $\int_0^t (T-V)dt$ for small changes in the q's shows that

$$\delta \int_0 (T-V)dt = \Sigma_1^n \left[\frac{\partial T}{\partial \dot{q}_i}\,\delta q_i\right]_0^t - \int_0^t \Sigma_1^n F_i \delta q_i dt \qquad (8)$$

where the F_i are the functions equated to zero in the Lagrangian equations (1). We shall assume that the functions T, V, q_1, q_2, . . . , q_n are of such a character that

(a) the expressions $\partial T/\partial \dot{q}_i$ all remain finite as the time increases indefinitely.

(b) the F_i for all values of the time can be developed in multiple Fourier series of the form given in (4).

From equation (8) and postulate (a) it follows that if the Lagrangian equations $F_i = 0$ are satisfied, the variation of the integral always remains finite, and by taking t very large we can then obtain the result that

$\delta(\bar{T}-\bar{V})=0$, or what is equivalent, $\delta F=0$, since the ν's are regarded as constants.

Conversely if $\delta F=0$, then the Lagrangian equations $F_i=0$ must be satisfied, for if $\delta(\bar{T}-\bar{V})$ vanishes the expression $\int_0^t \Sigma_1^n F_i \delta q_i dt$ is by postulate (a) finite for arbitrary large t. If we take $\delta q_i=\epsilon F_i$ where ϵ is a small quantity, it follows from (b) that the resulting variations in the q's are such as can be produced by altering the amplitudes A and B but holding fast the vibration frequencies ν_i. It is also seen by setting $\delta q_i=\epsilon F_i$, that the integral $\int_0^t \epsilon\ \Sigma_1^n F_i^2 dt$ always remains a finite quantity of order ϵ as the time increases indefinitely. Because of the periodicity properties assumed in (b) the F_i do not approach zero as the time becomes very large unless these quantities are always identically zero. Therefore the requirement that the limit $(t\to\infty)\int_0^t \Sigma_1^n F_i^2 dt$ is finite requires that the Lagrangian equations $F_i=0$ be satisfied for all values of the time. Consequently if the amplitudes are varied and the frequencies held fast, the equation $\delta F=0$ is a necessary and sufficient condition that the q's satisfy the Lagrangian equations.

We shall next show that Trkal's original quantum conditions given in (2) and also in (5) are equivalent to the requirement that δF vanish when the frequencies are varied but the amplitudes are held fast. By means of the Lagrangian equations or the equivalent variation principle given in (7) the amplitudes A and B are in general given as functions of n vibration frequencies $\nu_1, \nu_2, \ldots, \nu_n$ and n other arbitrary constants $\alpha_1, \alpha_2, \ldots, \alpha_n$. The ν's, which in general can each independently be assigned arbitrary values within some interval, together with the n α_i may be taken as the $2n$ arbitrary constants of integration.[13] When the explicit values of the A's and B's in terms of these $2n$ quantities are substituted in F, it would at first appear that F would become a function both of the ν's and α's. However, it follows immediately from the discussion given in the preceding paragraphs that the classical dynamics require that $\partial F/\partial a=0$ for any parameter a which is independent of the ν's. Consequently F cannot involve any of the α's, and is a function only of the ν's. Trkal's original quantum conditions given in (5), which

[13] Dynamical systems may be encountered in which one or more of the vibration frequencies ν_i cannot be assigned arbitrary values, and in which there are consequently more than n constants of integration of the type α independent of the vibration frequencies. The simplest example is a linear oscillator, for which the vibration frequency is a fixed quantity independent of the initial conditions. The extension of Trkal's variation principle can be proved to be valid for systems of this character, but for brevity such cases are not specifically considered in the present article, and instead it is assumed that each frequency can independently be assigned an arbitrary value within some interval.

state that F is stationary with respect to any alteration in the constants of integration may therefore be written in the form

$$dF/d\nu_k=0; \quad (k=1, 2, \ldots, n) \tag{9}$$

In Eq. (9), F is regarded as a function of the ν's rather than of the A's, B's, and ν's, for the A's and B's have here been expressed as functions of the ν's by solving the Lagrangian equations or using the variation principle (7). Let us now instead consider the A's and B's as undetermined and regard F as a function of the ν's, A's, and B's. If we then denote by $\partial/\partial\nu_k$ a differentiation with respect to ν_k in which the A's and B's appearing in F are held fast rather than treated as functions of the vibration frequencies it will be shown that the relations

$$\partial F/\partial\nu_k=0, (k=1, 2, \ldots, n) \ldots \text{i.e. } \delta F=0 \quad \begin{matrix}(\text{frequencies varied,}\\ \text{amplitudes held fast})\end{matrix} \tag{10}$$

follow immediately from (9). To do this let us replace each A $(\nu_1, \nu_2, \ldots, \nu_n)$ by A $((\nu_1+a_1, \nu_2+a_2, \ldots, \nu_n+a_n)$ and each B $(\nu_1, \nu_2, \ldots, \nu_n)$ by B $(\nu_1+a_1, \nu_2+a_2, \ldots, \nu_n+a_n)$ where the a's are arbitrary parameters. This substitution is legitimate, for it can be proved that this alteration does not affect the convergence of the series for the q's. Since, after solution of the equations of motion F involves the ν's not only directly but also implicitly through the A's and B's, we have

$$\frac{dF}{d\nu_k}=\frac{\partial F}{\partial \nu_k}+\left[\frac{\partial F}{\partial a_k}\right]_{(a_i=0) \quad (i=1, 2, 3, \ldots, n)} \qquad (k=1, 2, \ldots, n)$$

Now $\partial F/\partial a_k$ must equal zero since we have shown in the preceding paragraph that the classical dynamics require that δF vanish when the amplitudes are varied and the frequencies are held fast, and hence we may conclude that (9) implies (10).

It has been shown that the equations of classical mechanics will be satisfied if δF vanish when the amplitudes in the Fourier expansion of the q's are varied and the amplitudes are held fast (cf. (7)), while by (10) the Trkal or Sommerfeld quantum conditions are equivalent to the restriction that $\delta F=0$ when the vibration frequencies are varied and the amplitudes are regarded as constant. Combining these requirements we see that δF must vanish for any variations of the q's which can be produced by altering either the amplitudes or the frequencies in the multiple Fourier expansion of these coordinates. The single Eq. (6) therefore embodies all the demands of the classical dynamics and the quantum conditions, and may be regarded as the quantum theory version of Hamilton's Principle for a conditionally periodic system. The restriction that the variational orbits be capable of representation by Fourier series, which is a limitation not found in the ordinary Hamilton's Prin-

ciple, is not surprising, for otherwise the vibration frequencies lose all meaning, and no theory of quantization has yet been developed for such cases.

It is interesting to note that while the extended variation principle requires that the quantity F be stationary (i.e. $\delta F=0$), F is usually neither a minimum or a maximum. Instead in most cases it appears to be a minimum with respect to alterations in the amplitudes (the classical mechanics part of the variation principle) but a maximum with respect to variations in the frequencies (the quantum theory portion of the theory). If the orbits are to conform to relativistic rather than Newtonian mechanics, the extension of Trkal's variation principle given in Eq. (6) is still valid if in the expression F the kinetic energy T be replaced by $2\psi-T$, where the function ψ is defined in the footnote.[9]

Application of the Extended Variation Principle to a Non-Linear Oscillator

The extension of Trkal's variation principle developed in the preceding paragraphs can perhaps be more readily understood if an example is given showing how it is applied to a specific problem. Let us therefore consider a one-dimensional oscillator in which the restoring force is symmetric about the origin, so that the potential V involves only even powers of the displacement x from the equilibrium position. Instead of considering a linear oscillator, which has a potential of the form $V=\frac{1}{2}ax,^2$ we shall assume that there is a small perturbative term proportional to x^4. We have then

$$V=\tfrac{1}{2}a(x^2+\mu x^4); \qquad T=\tfrac{1}{2}m\dot{x}^2.$$

As there is only one degree of freedom, there can be only one vibration frequency, and the expansion for x given in (4) may be written in the form

$$x=A_1\cos(2\pi\nu t-\epsilon_1)+A_2\cos(4\pi\nu t-\epsilon_2)+\ \ldots\ . \qquad (A_1\neq 0)$$

We shall assume that the coefficients A_1, A_2. A_3,—and the frequency ν can be developed as power series in the small parameter μ. Since a linear oscillator (given by $\mu=0$) is characterized by an absence of harmonics, the amplitudes A_2, A_3, A_4, ..., must be of the first or higher order with respect to μ. If we substitute the above expression for x into the formulas for T and V and take the time averages of these quantities, which are most readily obtained as the constant terms in Fourier expansions, we find without difficulty that the function F defined in (3) has the value

$$F=\pi^2m\nu^2(A_1^2+4A_2^2+9A_3^2+\ \ldots)-\tfrac{1}{4}a(A_1^2+A_2^2+A_3^2+\ \ldots)$$
$$-(3/16)\mu aA_1^4-\tfrac{1}{4}\mu aA_1^3A_3\cos\epsilon-nh\nu \qquad (11)$$

where $\epsilon=3\epsilon_1-\epsilon_3$. In (11) terms in the "perturbative potential" $\frac{1}{2}\mu ax^4$

involving third and higher powers of μ have been neglected. The variation principle (6) requires that

$$\frac{\partial F}{\partial \nu}=0,\ \frac{\partial F}{\partial \epsilon}=0,\ \frac{\partial F}{\partial A_1}=0,\ \frac{\partial F}{\partial A_2}=0,\ \frac{\partial F}{\partial A_3}=0,\ \frac{\partial F}{\partial A_4}=0,\ \ldots$$

After computation of the various derivatives it is found that this series of equations becomes respectively

$$2\pi^2 m\nu\,(A_1^2+4A_2^2+9A_3^2+\ \ldots\ )-nh=0, \tag{12}$$

$$\tfrac{1}{4}\mu a A_1^3 A_3 \sin\epsilon=0, \tag{13}$$

$$2\pi^2 m\nu^2 A_1-\tfrac{1}{2}aA_1-\tfrac{3}{4}\mu a A_1^3-\tfrac{3}{4}\mu a A_1^2 A_3\cos\epsilon=0, \tag{14}$$

$$(8\pi^2 m\nu^2-\tfrac{1}{2}a)A_2=0, \tag{15}$$

$$(18\pi^2 m\nu^2-\tfrac{1}{2}a)A_3-\tfrac{1}{4}\mu a A_1^3\cos\epsilon=0, \tag{16}$$

$$(2k^2\pi^2 m\nu^2-\tfrac{1}{2}a)A_k=0 \qquad (k=4,\ 5\ \ldots\ \infty). \tag{17}$$

If we set $\mu=0$, the oscillator becomes linear, and the solution of the preceding system of equations takes the very simple form

$$\nu=\frac{1}{2\pi}\sqrt{\frac{a}{m}};\quad A_1=\sqrt{\frac{nh}{2\pi^2 m\nu}}=\sqrt{\frac{nh}{\pi m^{\frac{1}{2}}a^{\frac{1}{2}}}};\quad A_j=0\ (j=2,\ 3,\ 4,\ \ldots\ \infty).$$

The above expression for the vibration frequency, and the absence of harmonics (indicated by the relation $A_j=0$, $[j>1]$) are immediately recognized as characteristic of a linear oscillator, while the condition on A_1 effects a quantization of the amplitude. The corresponding value of the energy is given by

$$W=\bar{T}+\bar{V}=\tfrac{1}{4}(4\pi^2 m\nu^2+a)A_1^2=\tfrac{1}{2}anh/m^{\frac{1}{2}}a^{\frac{1}{2}}\pi=nh\nu$$

This is the familiar formula for the energy of a quantized linear oscillator and therefore all the characteristic properties of such a dynamical system can be derived from the single variation principle (6).

If we remove the restriction $\mu=0$, so that the oscillator is no longer linear, all of the harmonics except that corresponding to the amplitude A_3 still vanish to within the order of approximation under consideration, as Eqs. (15) and (17) require that $A_2=0$, $A_k=0$, $(k=4,\ 5,\ 6,\ \ldots,\ \infty)$. The amplitude A_3 may be determined with sufficient accuracy by substituting in (16) the approximate (i.e., unperturbed) value $a^{\frac{1}{2}}/2\pi m^{\frac{1}{2}}$ for the vibration frequency. We then have

$$A_3=(1/16)\mu A_1^3\cos\epsilon \tag{18}$$

Since A_1 and A_3 do not vanish, (13) demands that $\epsilon=\tau\pi$, where τ is an integer.

With the aid of the relations derived in the preceding paragraph, the elimination of ν between (12) and (14) gives

$$A_0^4=A_1^4(1+\tfrac{3}{2}\mu A_1^2+\tfrac{3}{32}\mu A_1^4)\,(1+\tfrac{9}{256}\mu^2 A_1^4)^2 \text{ where } A_0^4=n^2h^2/\pi^2 ma. \tag{19}$$

The solution of (19) for A_1^2 as a power series in μ is

$$A_1^2 = A_0^2(1 - \tfrac{3}{4}\mu A_0^2 + \tfrac{3}{2}\tfrac{3}{5}\tfrac{9}{6}\mu^2 A_0^4 + \ . \ . \ .),$$

whereby (14) and (18) become

$$\nu = \tfrac{1}{2\pi}\sqrt{\frac{a}{m}}(1 + \tfrac{3}{4}\mu A_0^2 - \tfrac{5}{6}\tfrac{1}{4}\mu^2 A_0^4 + \ . \ . \ .); \ A_3 = \tfrac{1}{16}\mu A_0^3 \cos(\tau\pi) + \ . \ . \ .$$

The final formula for the orbits is

$$x = A_0(1 - \tfrac{3}{8}\mu A_0^2 + \tfrac{3}{5}\tfrac{0}{1}\tfrac{3}{2}\mu^2 A_0^4 + \ . \ . \ .)\cos(2\pi\nu t - \epsilon_1)$$
$$+ A_0(\tfrac{1}{16}\mu A_0^2 + \ . \ . \ .)\cos(6\pi\nu t - 3\epsilon_1) + \ . \ . \ .$$

The expression for the energy, correct to terms of the second order in μ, is

$$W = m\pi^2\nu^2(A_1^2 + 9A_3^2) + \tfrac{1}{4}a(A_1^2 + A_3^2) + \tfrac{3}{16}\mu a A_1^4 + \tfrac{1}{4}\mu a A_1^3 A_3 \cos\epsilon$$

Substitution of the values obtained for A_1, A_3, and ν gives the final formula

$$W = a(\tfrac{1}{2}A_0^2 + \tfrac{3}{16}A_0^4\mu - \tfrac{1}{1}\tfrac{7}{2}\tfrac{7}{8}A_0^6\mu^2 + \ . \ . \ .); \ (A_0^2 = nh/\pi m^{\frac{1}{2}}a^{\frac{1}{2}})$$

The preceding solution may, of course, be verified by actually computing the perturbed orbits as solutions of the Newtonian equations of motion and then employing the Sommerfeld quantum conditions. The single variation principle (6) has therefore determined the character of the orbits in accordance with the conventional mechanics and simultaneously effected the proper quantization. For practical calculations in many problems there are usually other methods of computation which will give the correct quantized solution of the differential equations of motion more easily than the extension of Trkal's variation principle, but the latter is nevertheless of interest as combining formally the classical dynamics and quantum conditions in a single equation.

HARVARD UNIVERSITY,
May 9, 1923.

RADIATION POTENTIALS OF ATOMIC HYDROGEN

By P. S. Olmstead and K. T. Compton

Abstract

Atomic hydrogen was produced by thermal dissociation of molecular hydrogen with a tungsten furnace which could be maintained at 2800°K during observations. Electrons were emitted from an equipotential oxide coated platinum rod thrust into the furnace. Radiation was excited by electrons falling through an accelerating difference of potential between the rod and the equipotential tungsten cylinder forming the wall of the furnace, and was detected by its photoelectric action on a platinum disk placed beyond the open end of the furnace. This disk was shielded from ions produced in the furnace by an intervening set of charged plates. Radiating potentials were observed at 10.15, 12.05, 12.70, 13.00, 13.17, 13.27 volts, with additional radiation at the ionizing potential 13.54 volts. Within the probable error of the observations, less than 0.05 volt, the agreement with the Lyman spectral series and with the Bohr theory is exact.

Introduction

During the last few years various papers[1] have put closer and closer limits on the various radiating and ionizing potentials of hydrogen. Each successive paper has brought forward a new method or an improvement on an old one to separate ionization from radiation effects, and, in the more recent papers, to separate atomic from molecular effects. Bohr's theory of the hydrogen atom has been closely verified by this work, though the experimental curves have never set the radiation or ionization potentials to a greater degree of accuracy than tenths of a volt. For this reason the authors decided to study one phase only of the problem, namely, radiation from the hydrogen atom. This means that our apparatus must be highly selective. It must be free from all effects due to the hydrogen molecule, and, in addition, no effects due to ionization of the atom should be observed. This gives an opportunity

[1] Davis and Goucher, Phys. Rev. **10**, 101, 1917;
Bishop, Phys. Rev. **10**, 244, 1917;
Foote and Mohler, J. Opt. Soc. Amer. **4**, 49, 1920; Bur. Stan. Sci. Papers No. 400;
Horton and Davies, Roy. Soc. Proc. A **97**, 23, 1920;
Franck, Knipping and Kruger, Ber. D. Phys. Ges. **21**, 728, 1920;
Found, Phys. Rev. **16**, 41, 1920;
Compton and Olmstead, Phys. Rev. **17**, 45, 1921;
Boucher, Phys. Rev. **19**, 189, 1922;
Olmstead, Phys. Rev. **20**, 613, 1922;
Duffendack, Phys. Rev. **20**, 665, 1922;
Olson and Glockler, Proc. Nat. Acad. Sci. **9**, 122, 1923.

to find out whether there is one resonance potential for the hydrogen atom or several, corresponding, respectively, to the lines of the Lyman series. The paper by Olson and Glockler, mentioned in the note, gives this information, but with the heat of dissociation of the molecule included. Our paper, however, deals with a method which is more fundamental, and, in this way, eliminates many of the difficulties of Olson and Glockler and avoids all uncertainty in interpretation. We have measured the radiation potentials of the atom alone. To determine the heat of dissociation would be an entirely separate problem.

Apparatus

To solve the problem mentioned it was necessary for the apparatus to have the following two important features; first, hydrogen must exist only in the atomic state in the part of the apparatus in which the experiment is taking place; second, the receiving electrode must detect *only* radiation. These two factors involve several others. In order to obtain atomic hydrogen only we must be able to change all molecular hydrogen into atomic hydrogen in the region of the reaction. We must also be able to keep out effects due to positive or negative ions or electrons.

The first of these difficulties was overcome by using a tungsten furnace similar to one previously described.[2] It consisted of a cylinder of tungsten foil .001 inch in thickness stretched between two nickel-plated iron electrodes, each of which was water-cooled. It was about 4 cm long and 1 cm in diameter. Using a current of 150 amperes the potential drop in the furnace was 4.5 volts. The temperature near the center of the furnace could be maintained at 2800°K for a time long enough to make observations. This was sufficient to keep more than 99 per cent of the hydrogen in the furnace in a dissociated condition,[3] since the pressure was only a few hundredths of a millimeter.

For this problem an improved method of accelerating the electrons was used (see Fig. 1). For the source of electrons a single platinum wire was thrust into the furnace. The tip of this wire was hammered down to give as large a surface as possible, and then was coated with the Wehnelt oxides. This made it possible to get from an equipotential point a large emission of electrons due to the heat of the furnace. The emission could be increased or diminished by regulating the distance the point extended into the furnace. Inside the tungsten cylinder, constituting the furnace, a second cylinder, 7 mm in diameter was placed and connected electrically with one end of the furnace so that an accelerating

[2] K. T. Compton, J. Opt. Soc. Amer. and Rev. Sci. Inst. **8**, 910, 1922
[3] Duffendack, loc. cit.[1]

potential could be applied between the platinum point and this inner cylinder. Since both these are equipotential surfaces, no corrections due to potential drop have to be applied to the experimental results, leaving only that due to the distribution of velocities of the electrons. As stated in a recent paper[4] this is an important factor only in the case of very intense effects, and is not large in the present case since moderate tem-

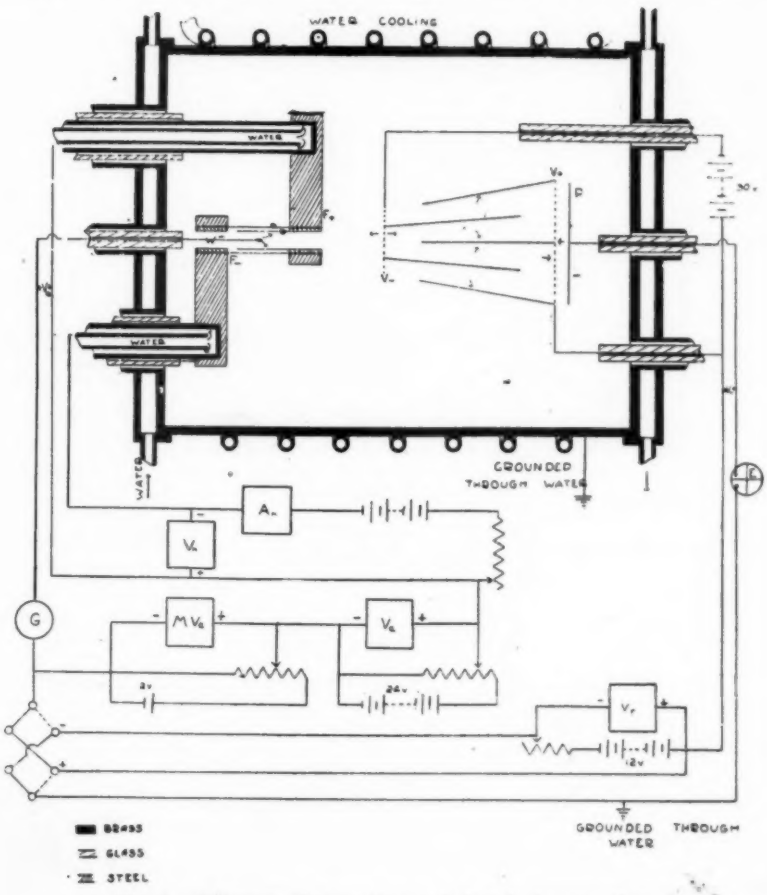

Fig. 1. Diagram of apparatus and electrical connections

peratures gave adequate emission from the oxide coated wire. This will be discussed further in studying the experimental results.

To detect the radiation resulting from collisions of the electrons and the hydrogen atoms, a plate was placed at the end of the furnace and perpendicular to it. A potential was applied to draw the photoelectrons from the plate, the effects being observed by means of a Compton electrom-

[4] Olmstead, Phys. Rev. 20, 613, 1923

eter. However, since positive or negative ions or electrons might register in addition to the radiation, a set of fins, charged alternately positively and negatively, patterned after those used by Kurth,[5] was placed between the end of the furnace and the plate. This made it possible to observe the effect of radiation only.

The various potentials were applied in the usual way for a four element tube. The furnace was placed so that its positive end was at the same potential as the inner cylinder. This made it impossible for any electrons to be accelerated from the platinum point through a higher potential drop than that between the platinum point and the equipotential cylinder.

Experimental Results and Discussion

Three examples of the experimental results are given in Figs. 2, 3 and 4. Each of these curves represents a stage in pushing the problem to its successful solution. Fig. 2 is the first curve which was taken, and, as may be seen, it was found that several breaks due to the atom were

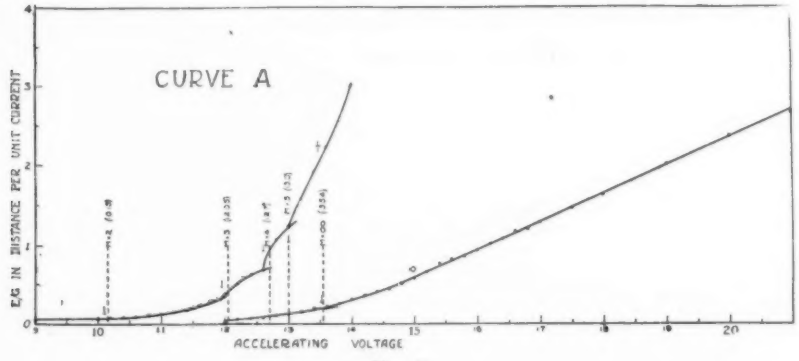

Fig. 2

definitely indicated, but effects due to the molecule, which are usually very strong, were entirely missing. No ionization effects were observed. In the case of the molecule we ordinarily expect an effect due to dissociation of the molecule plus ionization of one atom at about 16 volts. In the figure this part of the curve is very nearly a straight line. Effects which are due to dissociation of the molecule and radiation from one of the atoms, would be at potentials in the neighborhood of 12.6, 14.6, 15.2, etc. Using the data of Olson and Glockler the values would be even higher. No indication is found of any of these lines. This shows that our tube is entirely free from any effects due to the hydrogen molecule.

[5] Kurth, Phys. Rev. **18**, 462, 1921

Unfortunately, before we had an opportunity to study further the phenomenon given by our first experimental curve, we were forced to postpone our work because the furnace burned out and had to be replaced. This was quite a delicate operation, and it was a considerable length of time before we could proceed with the work.

Fig. 3 gives one of the first curves taken when the apparatus had been set up again. In this it was seen that the breaks were not nearly as sharp as might be expected from the results given in Fig. 2. After studying this curve and several more like it, for a short time, we found the cause to be that in replacing the furnace, we had turned it around end for

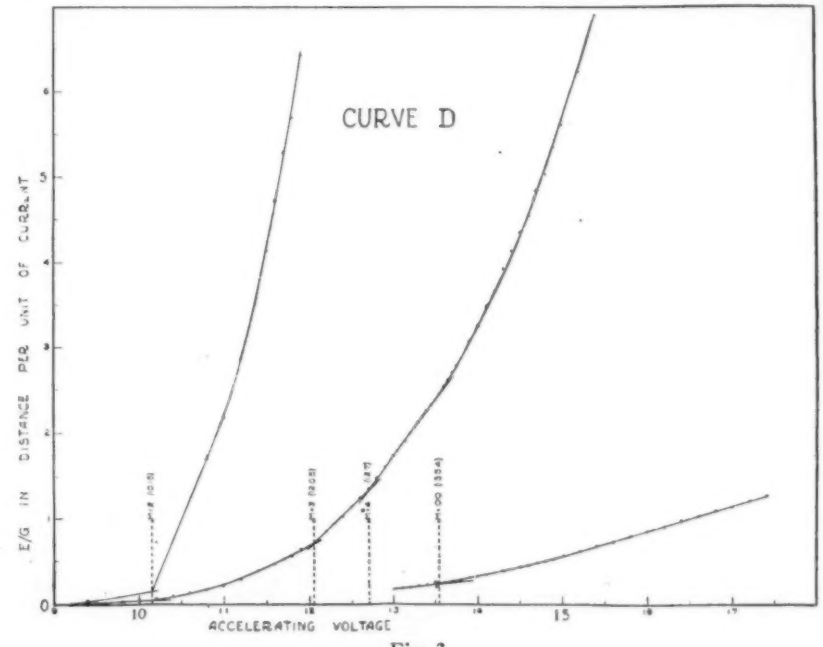

Fig. 3

end, and had thus interchanged the potentials. This made it possible for some electrons to be accelerated by more than the potential between the equipotential point and the equipotential surface, This means that the electrons emitted by the point would have a wider range of velocities, and that breaks due to them would not be as sharp as in the case of Fig. 2.

The obvious correction to make was to interchange the leads of the furnace and make it impossible to get a greater fall of potential than that between the two equipotential surfaces. This was done in the curves for which Fig. 4 is typical. In this curve the breaks are remarkably sharp.

The first break is different in shape from the others. It corresponds to an electron fall from the second orbit to the first, giving the first line of

the Lyman series. On first thought one would say that this effect should be a very strong one, but the curve shows that the second break which corresponds to a fall from the third to the first orbit is more marked than the first. It is well known that the first line of the Balmer series, but not the other lines, is almost always obtained reversed spectroscopically in an electron discharge tube.[6] This is similar to what happens in this case. Only a small amount of the radiation actually formed reaches the plate of the tube; the rest is taken up and re-emitted by other hydrogen atoms, and in this way is dispersed to various parts of the tube. This, ap-

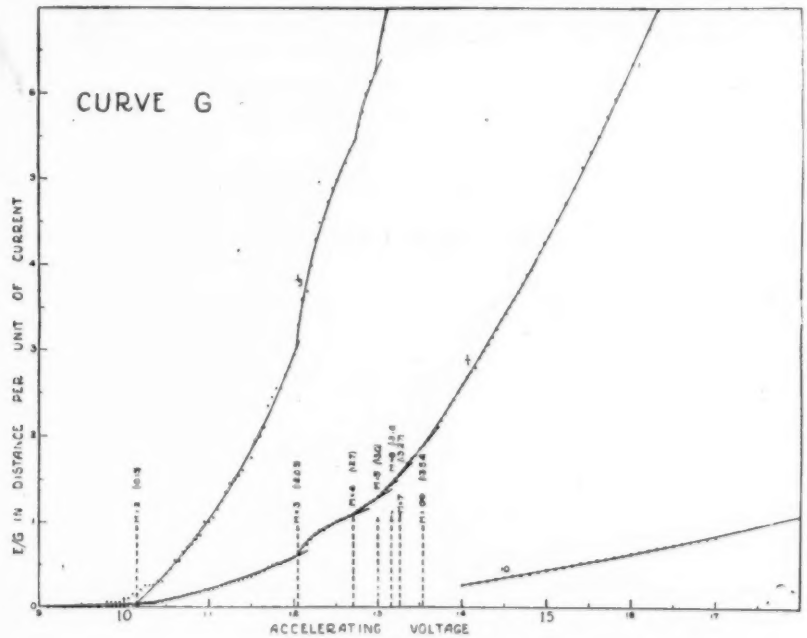

Fig. 4

parently, answers the question of Olson and Glockler about where the first line of this series should appear, and why they do not observe it as one of their breaks.

This radiation was found gradually to increase from zero with increase in electron velocity above the critical value. This is due, in part, to the distribution of velocities of the electrons. Some will have velocities greater than the average and thus will tend to start the effect before the point at which the average electron gives the effect. The way in which this works is given more in detail in a previous paper.[7] To elim-

[6] See, e.g., Wood's Physical Optics
[7] Olmstead, loc. cit.[4]

inate the effect of this distribution the best straight lines are drawn on either side of the break to determine the break point. In the case of breaks other than the first, the effect due to the distribution of velocities is very small. In other words, the average electron is the one that counts in giving an added effect. The faster and slower electrons produce the same effect as before, but when this is added to some original effect the weight of these electrons is discounted.

The presence of the break at a point corresponding to the ionization potential of the atom needs explaining. As this is a converging frequency of all lines in the Lyman series, this break might be taken as the sum effect of all radiations beyond those definitely indicated, which cannot be separately picked out. A better explanation, perhaps, is that this increase is in conformity with the well-known fact that the spectrum of hydrogen comes out much stronger after reaching the ionizing potential,[8] due partly to the more favorable distribution of potential between the electrodes, which increases all radiations. In fact, until the ionization potential is reached, only the first line of the Lyman series has been observed spectroscopically. This work shows, however, that it should be possible to get each line of the series to appear at its own characteristic potential. It has been assumed hitherto that the potential corresponding to the first line was the resonance potential, but in view of this work it seems that there are several resonance potentials, each of which corresponds to a line of the Lyman series.

This work has given a further check on the Bohr picture of the hydrogen atom in that the first six lines and converging frequencies of the Lyman series, corresponding to 10.15, 12.05, 12.70, 13.00, 13.17, 13.27 and 13.54 volts have been experimentally determined. In addition, it has opened the whole field of radiation potentials to closer investigation. The method, as outlined, is especially applicable for the study of radiation from the atom in the case of diatomic gases. The authors are at present investigating nitrogen, and will probably continue with other gases.

This work was performed in the Palmer Physical Laboratory at Princeton.

RESEARCH LABORATORIES OF THE AMERICAN TELEPHONE AND
TELEGRAPH COMPANY AND THE WESTERN ELECTRIC COMPANY, INCORPORATED,
NEW YORK CITY (P. S. Olmstead).

PALMER PHYSICAL LABORATORY,
PRINCETON, N. J. (K. T. Compton),
May 29, 1923.

[8] For instance, Hughes and Lowe, Phys. Rev. **21**, 292, 1923

THE DETERMINATION OF THE TIME BETWEEN EXCITATION AND EMISSION FOR CERTAIN FLUORESCENT SOLIDS

By Philip F. Gottling

Abstract

Time lag between excitation and emission of fluorescence by barium platino-cyanide and rhodamine.—The work begun in 1921 by R. W. Wood on the measurement of fluorescent intervals and phosphorescent times has been continued. The method of Abraham and Lemoine, somewhat modified, was used for determining the very short periods of time involved. The fluorescent light is polarized and then passed through a condenser, containing nitrobenzene as dielectric, which had begun to be discharged when the illuminating spark started. The later the light arrives the lower the average field of the condenser and the smaller the angular setting of the analyzing nicol to match the two images produced by a double image prism. The apparatus was calibrated by means of light reflected from a mirror at different distances from the spark. The interval of time between the occurrence of a spark and the emission of the fluorescent light excited by that spark, was found to be $(2.12 \pm .01) \times 10^{-7}$ sec. for barium platino-cyanide and $(2.11 \pm .14) \times 10^{-8}$ sec. for rhodamine.

Introduction

IT HAS been shown recently[1] that some fluorescent substances remain dark during a definite period of excitation, in other words, that the exciting energy was imprisoned for a short but definite and measurable interval of time within the fluorescent substance. In the case of mercury vapor, the period intervening between the beginning of the process and the emission of the light was found to be about 1/15000 sec. Similar observations made with barium-platino-cyanide indicated that not only was this interval of time less than 1/400,000 sec. but, furthermore, that the total duration of the phosphorescence, after the exciting incident energy ceased to fall upon the fluorescent substance, was also very short.

It was evident that the period of darkness for barium platino-cyanide was outside the range of the synchrono-phosphoroscope method employed. Some preliminary experiments were made employing the method of Abraham and Lemoine.

[1] R. W. Wood, Proc. Roy. Soc. A. **99**, 362, 1921.

This method[2] makes use of the double refractive property of liquids when subjected to an electrostatic field. A condenser formed by immersing two metal plates in a liquid such as carbon bisulphide or nitrobenzene, is allowed to discharge through a spark gap. A Nicol prism is placed between the spark gap and the condenser, and, if the spark is viewed through the space between the condenser plates, it is impossible to extinguish the light by a second Nicol held close to the eye, unless the path over which the light must travel before reaching the condenser is increased the right amount, for example, by reflection in a mirror placed at the right distance.

It is evident from this that the double refraction of the liquid under these conditions varies with the time. This circumstance may be employed to measure the time which expires between the instant of occurrence of the spark and the beginning of the fluorescent light which its radiation excites, by adjusting the position of the mirror so that the fluorescent light just does not pass through the second or analyzing Nicol. The distance between this position and the corresponding position when the light from the spark is at the point of extinction, when divided by the velocity of light, would give the time the fluorescent substance remains dark.

Description of Apparatus

For the particular problem at hand, however, it was found advantageous to elaborate on the simple arrangement and method just described by introducing a double image prism into the optical path of the light between the condenser and analysing Nicol. The final electrical circuit and optical arrangement employed is indicated by Fig. 1, an arrangement very similar to that proposed by Lord Rayleigh for the measurement of very short times.[3]

The spark gap P was connected through a resistance R to the condenser K containing nitrobenzene, which will be referred to as the Kerr cell. The latter alone gave a poor spark, but by connecting a Leyden jar A in parallel with the first circuit, as shown in the figure, a brilliant spark was obtained. The condensers A and K, charged intermittently by an ordinary spark coil C operated by a twelve volt storage battery, were discharged at the spark gap P. The capacity of the Kerr condenser was 49.7×10^{-11} farad. The inductance L of the K-R-P circuit was approximately 1100 cm, and the value of the resistance R was usually greater than 100 ohms. With 300 ohms as the resistance R, the time constant

[2] Abraham and Lemoine, Compt. Rend., p. 206, 1899

[3] Rayleigh, Scientific Papers, Vol. V, p. 190

of the K-R-P circuit was 1.49×10^{-7} sec. The period of the spark and Leyden jar, i.e. the A-P circuit was 1.19×10^{-7} sec.

Light from the spark gap P was polarized by the Nicol N_1. The double image prism D was placed between the Kerr cell K and the analyzing Nicol N_2, and so orientated as to give only one image of the narrow slit S when K was disconnected from the electrical circuit. The Nicol N_2 was then turned to the position of extinction of this image. Call this the zero position of N_2. Introduction of the Kerr cell into the electrical circuit caused the restoration of one of the images, namely that one whose plane of vibration was parallel to the short diagonal of the analyzing Nicol. Turning N_2 through a small angle restored the other image, and two positions of N_2, obtained by turning it clockwise in

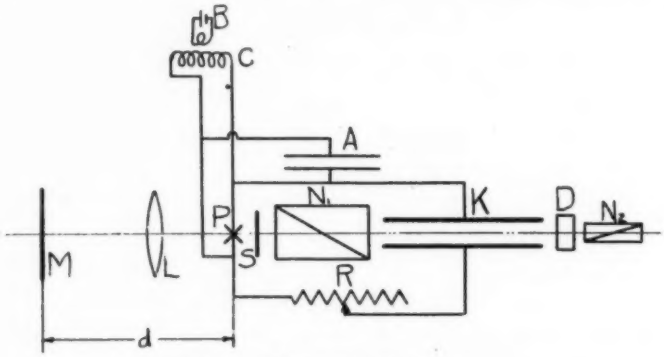

Fig. 1. Diagram of apparatus.

one case and counter clockwise in the other case, could be found at which the intensities of the two images appeared the same. The angles α through which N_2 must be turned to arrive at these positions, are opposite in direction and equal in value. If instead of illuminating the slit S by the spark directly, the light is first made parallel by a lens L, is reflected in a mirror M, and is then focused on the slit S, it is found that the angle α is different for different positions of the mirror M.

Theory

We will consider the electrical sequence of events of the circuits in Fig. 1 and the resulting optical effects. The interrupter of the primary circuit of the induction coil C induces a high potential in the secondary which in turn charges the condensers A and K. This charging process continues until the breakdown potential of the spark gap P is reached. At the occurrence of the spark, an oscillatory discharge of A through P begins, while the discharge of K through the resistance R and P is non-

oscillatory if, for the circuit K-R-P, $R^2/4L^2 > 1/LK$, where L is the inductance of the circuit and K the capacity of the Kerr condenser. This condition was maintained during the experiment. The electric field acting upon the nitrobenzene under these conditions will, therefore, vary with the time t in some such manner as shown in Fig. 2.

Now it may readily be shown that the setting α of the analyzing Nicol necessary for balance, depends upon the field strength alone and not upon the intensity of the light. This was also verified experimentally. Hence if the light train begins to pass through the condenser K at the instant t_1 (Fig. 2) when the field strength is E_1, the corresponding setting of the Nicol will be a function of the average value of the field which obtains from t_1 to the end of the light train. If the light begins to pass at some later instant t_2, the average field strength will be less and the setting of the Nicol will be correspondingly less. In order to determine the relation between α and t, the instant when the light begins to arrive was

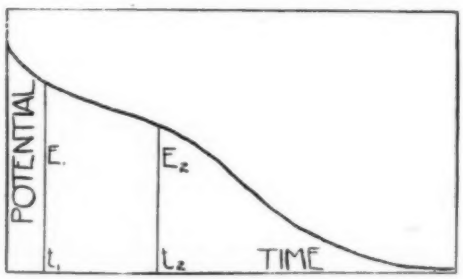

Fig. 2. Time variation of the potential across the Kerr condenser.

varied by varying the position of the mirror M from which the light has been reflected. If, then, light from some fluorescent solid placed close to the spark P is observed, a setting of the Nicol will be obtained which, when compared with the relation between α and t previously determined, will give the time lag between the excitation and emission of light for that substance.

Experimental Procedure

The method of measuring the dark time of any fluorescent substance is to determine the variation of 2α with the distance of the mirror M when some high resistance, as 1000 or 1500 ohms, is used as the damping resistance R, and to determine the difference between the angle 2α for the fluorescent substance in question and that obtained by viewing the spark directly under the same conditions. If this difference is large, say 5° to 10°, evidently the period of darkness for this substance is long, for with such a high resistance in the circuit described above, the angle 2α

varies by about five degrees as the mirror M is moved from the spark to a position 45 meters from the spark. For a case of this kind results obtained when R is two hundred ohms or less are not reliable since for such a low resistance the plates of the K-condenser discharge almost completely in the time required for light to travel ninety meters (see Curve E, Fig. 3), and the cell would consequently only slightly restore the fluorescent light, thus making it difficult if not impossible to balance

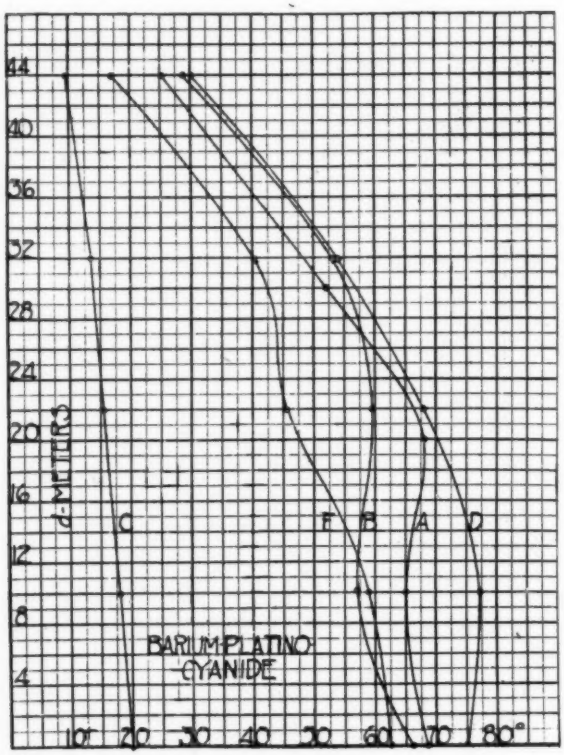

Fig. 3. Results with barium-platino-cyanide.

the intensities of the two images. In such a case the resistance should be kept as large as 400 ohms or more and the fluorescent light would be restored accordingly (see Curve C, Fig. 3).

If, however, with 1000 ohms in the circuit the angle 2α for the fluorescent substance examined differs by only a degree or two from the angle obtained from observations made directly on the spark, the time interval in question is of the order of magnitude of that required for light to pass twice the distance from the spark to a mirror about twenty meters away. In such a case lower resistance must be employed so as to increase

the rate of decay of charge on the plates of the Kerr cell and thus increase the rate of change of restoration of the cell.

The shape of the curves obtained showing 2α as a function of the distance between the spark and mirror, depends, in the electrical arrangement shown in Fig. 1, not alone upon the resistance R, but also upon the width of the spark gap. Curves A, B, D, E, Fig. 3, which were taken with a spark gap of approximately 1 cm, show oscillations. When the spark gap was reduced to 2 or 3 mm curves such as D, Fig. 4, were

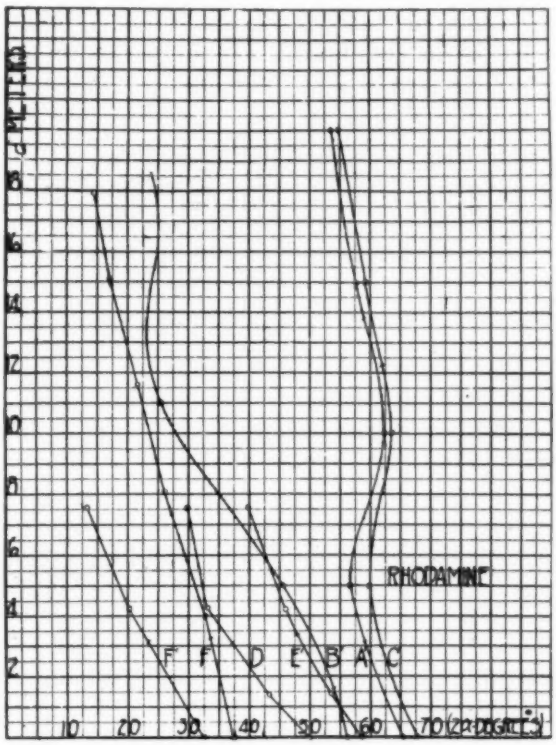

Fig. 4. Results with rhodamine.

obtained. In instances where the dark time is very short these oscillations are highly undesirable, for there are two and sometimes three points on the curve whose abscissas are the same angle 2α as obtained for the fluorescent substance. If, however, the resistance is changed, and another curve and angle 2α for the fluorescent substance is determined, there will again be two or three points on this new curve whose abscissas equal the new angle 2α for the fluorescent substance. One of these points only, however, will have the same ordinate as one of the three points of

the preceding curve, so that, even if the oscillations exist, it is still possible to determine a short time interval.

The method, therefore, is to determine approximately the interval with a high resistance R in the electrical circuit, and then more accurately with a lower resistance if necessary. The best conditions are obtained when the nature of the resulting curve is such as to have a rapid change in 2α in the region of the angle of the fluorescent substance. At the same time the latter angle should be not only fairly large, a circumstance which is consistent with brightness of the restored images, but should also differ by 10 or 15° from the angle obtained when viewing the spark directly; then the error in the determination of 2α for the fluorescent material gives a relatively small error in the dark time.

Results

Five determinations of the time interval between the absorption and emission of light in the case of barium-platino-cyanide were made, using four different resistances varying from 200 to 400 ohms. Curves A, B, C, D, E in Fig. 3 show the results. The abscissas of curve C are diminished by 40° to avoid crowding the curves. The following table gives the angle obtained in each case and the corresponding position of the mirror which would give the same angle as taken from the curve. Twice the average of these distances when divided by the velocity of light gives the dark interval for barium-platino-cyanide.

TABLE 1

Barium-platino-cyanide

Curve	R	Angle	Distance
A	300 ohms	48.7°	3180 cm
B	250	53.2	3196
D	300	54.1	3180
E	200	40.6	3169
			Mean 3181 cm

$T = 2d/v = 2\times 3181/3\times 10^{10} = (2.12 \pm .01)\times 10^{-7}$ sec.

The value of d obtained from curve C, although agreeing as well as could have been expected with the other values, was not used in calculating the mean, for in this case the resistance was 400 ohms and the curve so steep that a variation of $\frac{1}{2}$° in the angle results in a variation of 75 cm in the distance d. The maximum deviation from the mean value is about $\frac{1}{2}$ per cent. The time interval is $(2.12 \pm .01)\times 10^{-7}$ sec.

The next substance examined was rhodamine in a solution of acetone, acetic acid and glycerine. The fluorescence of rhodamine was bright red and no difficulty was experienced in matching intensities of the two images. The percentage accuracy in this case was, however, not as good

as in the case of barium-platino-cyanide. The mean value 316 cm for d yields $(2.11 \pm .14) \times 10^{-8}$ sec. as the period of dark time for rhodamine.

TABLE 2

Rhodamine

Curve	R	Angle	Distance
F	200 ohms	53.5°	325 cm
A′	150	59.0	313
B′	200	54.0	320
C′	100	62.0	303
D′	80	37.3	302
E′	80	47.9	338
F′	80	43.3	312

Mean = 316 cm

$T = (2.11 \pm .14) \times 10^{-8}$ sec.

The curves obtained in determining the time interval for rhodamine are shown in Fig. 4. Curve B' is there drawn to the same scale of abscissas as the other curves in the Figure but to half scale in the ordinates. The abscissas of F and F' are diminished by 20° to avoid crowding the curves. Particular attention is called to A' and C' which show the oscillations referred to above. In each of these cases there are three points whose abscissas are the angle 2α obtained from the observations made on rhodamine, the ordinate of only one of A' is the same as the ordinate of one of the three points of C′. This ordinate, moreover, agrees very well with those obtained from the curve showing no oscillations.

The author wishes to acknowledge his appreciation to Professor R. W. Wood for his valuable suggestions, and to Dr. Frank V. Grimm who prepared the nitrobenzene.

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May 16, 1923.

EFFECT OF HEAT TREATMENT ON THE PHOTO-ELECTRIC EMISSION FROM PLATINUM

By F. G. Tucker

Abstract

Effect of heat treatment on the photo-electric emission from platinum.—A thin Pt foil was mounted between heavy leads inside a Faraday cylinder in a pyrex tube with a quartz window sealed to it by means of a graded seal. The *threshold* or long wave-length limit λ_0 was determined by plotting the current per unit light intensity as a function of wave-length of the Hg arc line used. This threshold was found to vary with the previous heat treatment. Glowing the foil at 900°C for 8 hours gave repeatedly a value close to 2700 A; glowing for 4 or 5 hours at bright yellow heat decreased the emission greatly and shifted λ_0 to 2475 A. Immediately after glowing for 2 hours at a temperature of over 1400°C, the emission from the suddenly cooled foil was found to be zero even under the influence of the full radiation of the Hg arc; after 5 minutes the photo-emission began to appear and increased rapidly at first and then more slowly. Evidently the threshold for pure gas-free Pt must be below 1849 A and the effects ordinarily observed must be due to a gas film or some other film formed on the surface. This is also suggested by the shift of λ_0 to a longer wave-length, 2770 A, when the tube was baked at 200°C without glowing the foil.

Variation of photo-electric threshold for platinum with temperature to 600°C.—After a given moderate heat treatment of the foil, the threshold was found to be the same at 600° as at 20°. This indicates that the film responsible for the emission was unchanged and that the threshold under these conditions does not depend on the kinetic energy of the free electrons in the foil.

Introduction

THE recent work of Millikan[1] on the relation existing between the photo-electric limiting frequencies of two elements and their contact difference of potential has led to the very important conclusion that either the electrons emitted under the influence of light are free electrons, or the electron is able to escape from the atom with energy $h\nu$, where h is Planck's constant and ν is the frequency of the incident light. The present investigation grew out of an attempt to obtain additional evidence on the nature of photo-electrons, by studying the temperature variation of the photo-electric threshold of platinum which had been denuded of gases by glowing at high temperatures.

[1] Millikan, Phys. Rev. (2) **18**, 236, 1921

Apparatus and Procedure

The mounting of the emitting filament is shown in Fig. 1 and is essentially the same as used by Koppius[2] in his recent determination of the long wave-length limit of platinum. The filament F of platinum foil, 20 mm long, 5 mm wide and .0005 inch thick, is clamped and riveted to the copper jaws BB'. The leads AA' are 1/8 inch tungsten rods driven into holes bored in the jaws BB' and sealed directly into pyrex glass. C represents a copper-oxide Faraday cylinder which served to catch the emitted electrons. The cylinder wall is not perforated, but the hole O allows the incident radiation to fall upon the filament. Connection is made to the measuring electrometer by means of two tungsten wires, similar to E, which also support the cylinder.

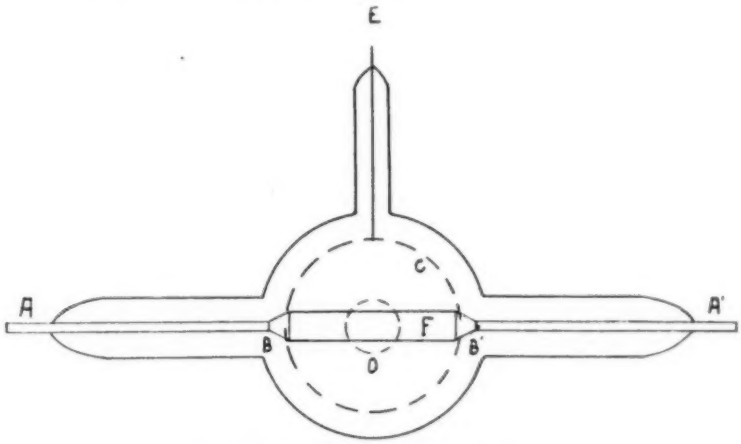

Fig. 1. Photo-electric tube.

In the original apparatus, the end of the pyrex tube, 40 mm in diameter, was closed with a quartz window cemented to the glass with a special cement kindly furnished by the Mantle Lamp Company of America. This joint was repeatedly baked for hours at 200°–225°C without impairing in the least the vacuum in the system. This tube was later replaced by a similar one built by the Cooper-Hewitt Electric Company, in which a window of clear fused quartz was sealed to a quartz tube 40 mm in diameter and about 2 cm long. By means of a graded seal[3] this quartz tube was in turn sealed to a pyrex one of the same diameter, and the emitting filament was mounted as before. This tube was baked at 450°C. The system was exhausted by a mercury diffusion pump working against an x-ray fore-vacuum produced by a Gaede rotary

[2] Koppius, Phys. Rev. (2) **18**, 443, 1921

[3] Engineering Dept. Bull. No. 104, Cooper-Hewitt Electric Co.

mercury pump. Pressures were measured with a Buckley ionization manometer[4] and the usual liquid air traps were inserted in the system to prevent the mercury vapor from diffusing over into the ionization gauge and the part of the tube containing the filament. The pumps were run continuously while the filament was being glowed and while measurements of photo-currents were being taken. In every case the manometer indicated a pressure between 1 and 10×10^{-6} mm of mercury.

A Cooper-Hewitt quartz mercury arc served as a source of illumination and monochromatic radiation of a desired wave-length was directed upon the filament by means of a Hilger monochromator. In order to test the purity of the lines resolved by this instrument, the emergent light was photographed with a large quartz spectrograph. For the principal mercury lines below λ2800, with the single exception of λ2650, the plates showed that only the line corresponding to the reading of the wave-length drum of the illuminator was transmitted. In the case of λ2650 there was a faint transmission of the line λ2640.

To determine the long wave-length limit, the photo-currents per unit intensity of the incident light were plotted as ordinates against wave-lengths as abscissas. The intercept of this curve upon the wave-length axis gave the limiting wave-length, and results by this method have been shown to agree, within the limits of experimental error, with the direct method of stopping potentials.[5] The relative intensities of the lines used for illuminating the target were measured by means of a sensitive thermopile and Coblentz galvanometer.[6] The results of these measurements are given in Table I.

TABLE I

Wave-length	Average galvanometer deflection
2800 A	4.9
2650	9.0
2536	11.7
2483	3.1
2400	1.5
2378	1.0
2300	.6

Before taking observations the tube was baked for five or six hours, at 200°C in the one case and at 450°C in the other. The filament was then glowed at various temperatures ranging from bright red to white heat, as indicated under results. The Faraday cylinder was main-

[4] Buckley, Proc. Nat. Acad. Sci. **2**, 683, 1916
[5] Millikan, Phys. Rev. (2) **7**, 355, 1916
[6] Souder, Phys. Rev. (2) **8**, 310, 1916;
Coblentz, Bull. Bur. Stds. **9**, 56, 1913

tained at a positive potential of 15 to 50 volts with respect to the filament and the photo-currents were measured with a quadrant electrometer having a sensibility of 1600 mm per volt. The quartz arc was mounted in an asbestos lined box and run at a high temperature as the work of Souder[6] showed that the radiant energy output was constant under these conditions. Throughout the experiments it was run at 117 volts and 2.72 amperes. A change of three per cent in the arc voltage could be readily detected in the photo-current.

Experimental Results

In each case the initial behavior of the filament was similar to that observed by Koppius,[2] viz., no appreciable emission could be obtained until after the filament had been glowed a few minutes at red heat. After a preliminary glowing at bright red heat for 8 hours, the long wave-length limit of the filament fell consistently at about 2700 A, as shown in Curve I, Fig. 2. The photo-currents varied from day to day but the

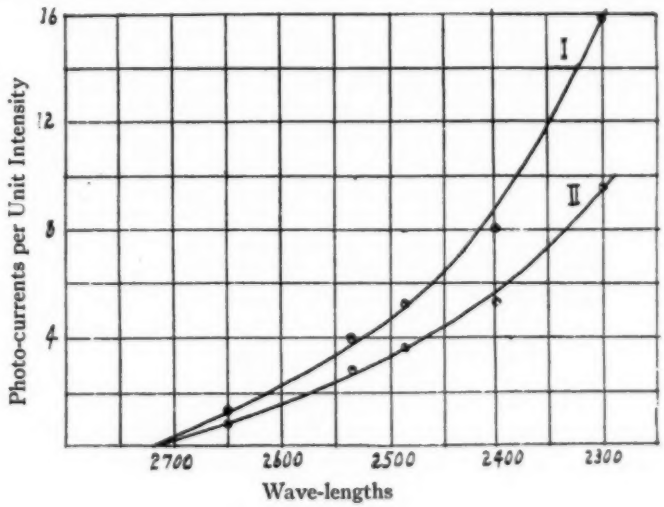

Fig. 2

threshold frequency remained practically constant as long as the filament was subjected to this particular type of preliminary heat treatment.

When the glowing temperature was increased, however, the value of λ_0 was shifted toward the shorter wave-lengths. Curve I, Fig. 3, is a typical example of the results obtained after heating the foil four or five hours at bright yellow heat. The emission had decreased to such an extent that it was necessary to double the slit width of the illuminator in order to get currents which would be accurately measured. The inter-

cept of Curve I gives a value of 2475 A for the long wave-length limit instead of approximately 2700 A which had been obtained consistently in previous observations. Allowing the filament to stand in a vacuum of 1×10^{-5} mm for 24 or 48 hours produced a large increase in the photo-current but the long wave-length limit was displaced only about 25 A.

In an endeavor to find the cause for the change in behavior of the filament, after obtaining the results shown in Curve I, Fig. 3, the tube was baked for three hours at 200°C and readings were taken without glowing the filament. These observations are shown in Curve II, Fig. 3. The photo-currents for the shorter wave-lengths were increased to ap-

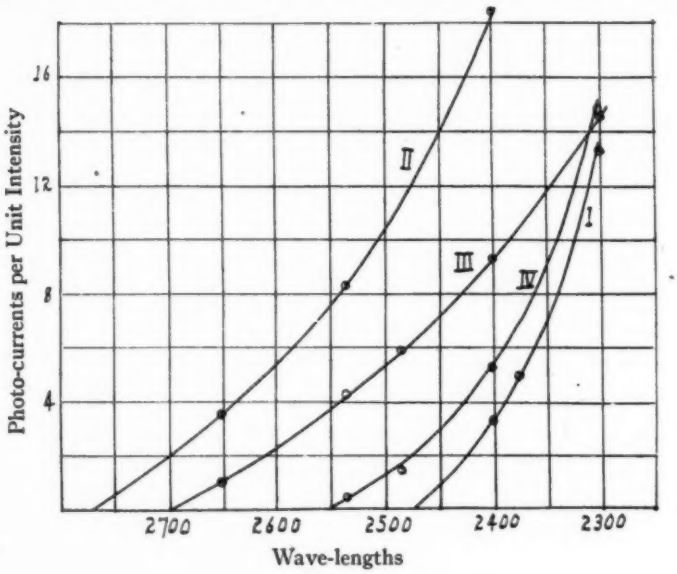

Fig. 3

proximately nine times the values obtained before the baking of the tube, and the intercept was shifted to 2770 A. After glowing the filament for 30 minutes at red heat Curve III was obtained which is practically identical with results obtained in the earlier part of the work. Glowing the foil another 30 minutes at white heat shifted the observations to those shown in Curve IV.

It is evident from these results that the gases given off by the copper-oxide cylinder during the baking out of the tube and the glowing of the filament, have a pronounced effect upon the photo-emission, and the value of the limiting frequency. Heating at temperatures of 800°–900°C is not sufficient to denude the foil of gases. Even after glowing at white heat the filament is very quickly covered with a film of gas sufficient to affect the electron emission. This was shown by the following experi-

ment. The filament was glowed several hours at white heat and then allowed to cool to room temperature, and immediately before taking an observation it was again glowed at white heat for 30 seconds. When illuminated with the line λ2300 there was no measurable electron emission, even after the slit of the monochromator had been opened to a width of 2.5 mm, which was four times the width regularly used. After an interval of three minutes the same illumination gave a deflection of 5 mm in 40 seconds and after five hours the deflection had risen to 100 mm. Another glowing for five minutes at white heat reduced the deflection to 1 mm.

In the earlier experiments with the improved tube, the results obtained with the first filament were verified. However, after the new filament had been subjected to several six hour glowings at bright yellow heat,

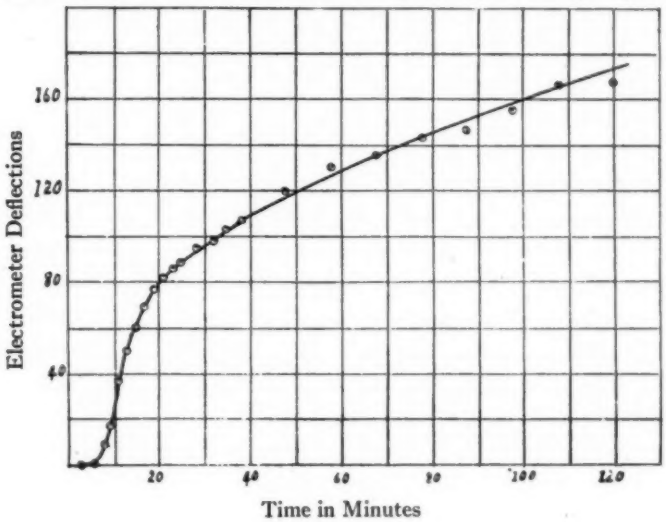

Fig. 4

it showed no emission under the influence of the radiation transmitted by the monochromator, even for wave-lengths down to 2000 A and with a slit width of 3.8 mm. The full light of the arc was then focused directly upon the filament and a moderately large emission was obtained.

A more careful study of the photo-current obtained under the influence of the unresolved light of the mercury arc revealed the following facts. After repeated glowings at bright yellow heat this emission persisted and showed a decided increase with time after glowing. When a five hour glowing at bright yellow heat was followed by heating the filament for two hours at a black body temperature of 1510°K, the photo-emission was practically zero for a few minutes after the heating current was stopped. Following this the emission increased, rapidly at first,

and then more slowly. A typical recovery curve is shown in Fig. 4 in which the ordinates are electrometer deflections in 40 seconds. After allowing the filament to recover for two hours another glowing at the same temperature caused it to reproduce the behavior shown in Fig. 4.

The temperature of the white hot filament was measured with an optical pyrometer, and since this instrument was sighted through the quartz window upon the bright platinum surface, the true temperature of the filament was approximately 150°–200°C[7] higher than the pyrometer reading. The true temperature of the filament, therefore, was approximately 1450°C.

In the earlier part of the investigation the threshold of platinum at a temperature of 600°C was determined. The observations shown in Curve II, Fig. 1 were taken immediately after those represented by Curve I. It is evident that the long wave-length limit is not shifted when the temperature of the foil is increased from 20°C to 600°C, although the photo-currents are decreased.

Discussion

From these observations it is evident that glowing at bright red or even yellow heat produces only a slight change in the gaseous layer upon platinum foil. The later experiments show that a temperature of approximately 1450°C is necessary to remove this film, or at any rate to modify it in such a manner that the surface is no longer photo-sensitive for radiation from a quartz mercury arc. We are led, therefore, to the conclusion that when a platinum surface is most free from gases (perhaps it can never be completely free) it exhibits no photo-electric emission for wave-lengths greater than 1849 A.[8] Sende and Simon[9] and also Suhrmann,[10] working in Hallwach's laboratory have recently arrived at the same conclusion concerning the photo-electric threshold of platinum.[11] Several earlier investigators,[12] on the other hand, working under less favorable conditions for denuding the foil of gases, have arrived at different conclusions.

The view that the intrinsic long wave-length limit of platinum is less than 1849 A receives additional support from the work of Kustner,[13]

[7] Bureau Standards Technical Paper No. 170, p. 113, 1921

[8] Hughes, Report on Photo-Electricity. Bull. Nat. Research Council **2**, 125, 1921

[9] Sende and Simon, Ann. der Phys. **65**, 697, 1921

[10] Suhrmann, Ann. der Phys. **67**, 43, 1922

[11] Since this was written an article has appeared by Welo, Phil. Mag. **45**, 593, 1923, in which the author concludes that gas free platinum is photo-sensitive for wave-lengths longer than 1849 A.

[12] Piersol, Phys. Rev. **8**, 238, 1916, gives detailed bibliography of earlier work

[13] Kustner, Ann. der Phys. **46**, 893, 1915

who found that newly distilled zinc showed no photo-emission under the influence of a quartz mercury arc. Further evidence is also furnished by Hughes'[14] study of the contact potential of zinc. This author found newly distilled zinc to be electro-negative to platinum but upon exposure to a trace of reacting gas it became electro-positive. In view of the relation existing between the photoelectric threshold of two elements and their contact difference of potential,[15] the results obtained by Hughes indicate that λ_0 for zinc is shifted toward the violet as the surface is denuded of gases.

At first sight this shift in the limiting frequency of platinum after glowing at high temperatures seems to destroy the numerical relationship,[15, 16] which has been shown to exist between the work function φ_0 for thermionic emission, and the function $h\nu_0$ for photo-electric emission. If, however, we substitute in the equation

$$eV = h\nu_0 = hc/\lambda_0.$$

$e = 4.77 \times 10^{-10}$; $h = 6.55 \times 10^{-27}$; $c = 3.00 \times 10^{10}$; and $\lambda_0 = 1850$ A, we find a value for V of 6.68 volts, while Langmuir[17] has obtained a value of 6.62 volts for ϕ_0 for platinum under very good conditions as to freedom from gases. Richardson,[18] on the other hand, is inclined to consider approximately 5.00 volts as the "best guess" for the thermionic work function of platinum.

The fact that after a moderate heat treatment of the foil, the threshold was found to be the same at 600°C as at 20°C does not enable us to draw any conclusions concerning the nature of photo-electrons. It can only be interpreted as indicating that the film responsible for the emission was not changed; and if the threshold is a function of the kinetic energy of the free electrons in the metal, the fact was completely masked by the much greater effect due to the surface film.

I take this occasion to express my appreciation to Professor Millikan for suggesting this problem and for his continued interest in the work, and to Professors Gale and Dempster for their many helpful suggestions, especially during the latter part of the investigation.

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August 26, 1922.[19]

[14] Hughes, Phil. Mag. **28**, 337, 1914
[15] Millikan, Phys. Rev. **18**, 242, 1921
[16] Richardson, Science N. S. **54**, 283, 1921
[17] Richardson, Emission of Electricity from Hot Bodies, Second Edition, p. 81, 1921.
[18] Richardson, Ibid. p. 87
[19] Received May 22, 1923—Ed.

COEFFICIENTS OF SLIP AND MOMENTUM TRANSFER IN HYDROGEN, HELIUM, AIR AND OXYGEN

By Edward Blankenstein

Abstract

Coefficients of slip for polished silver oxide surfaces in hydrogen, helium, air and oxygen.—The rotating cylinder method was used, and besides taking precautions to insure spectroscopically pure gases, a continuous circulation of gas was maintained to minimize the effect of the release of occluded gas from the walls of the apparatus. The mean values reduced to 23°C and 76 cm Hg, are: 121(H_2); 190(He); 68.5(Air); 72.1(O_2), all times 10^{-7} and accurate to about one per cent. *Maxwell's coefficient of diffuse reflection f* comes out 1.00, 1.00, .98, and .99 for the four gases. To check these results, measurements of the variation of the deflection with pressure were made at low pressures, .0003 to .0015 mm, where the mean free path is considerably greater than the distance between the cylinders. From a comparison of these results with the slopes computed from kinetic theory assuming complete diffuse reflection, f comes out 0.99, 0.99, 0.97 and 0.96 for the four gases, in good agreement with the values given by the slip measurements. The intercepts for zero pressure indicate the presence of some vapor, but this should not affect the slopes appreciably. It is concluded (1) that for these gases practically all molecules are diffusely reflected from the surfaces used, the percentages specularly reflected being close to zero for H_2 and He, and about 2 or 3 for air and O_2; also (2) that values of f deduced from Maxwell's equation of slip are reliable.

Introduction

FROM the kinetic theory of gases Maxwell deduced that the coefficient of viscosity should be independent of the pressure, and experimental investigations verified this deduction over a wide range of pressures. At very low pressures, however, the viscosity becomes less than at the higher pressures and this deviation is of interest because it may be connected theoretically with the nature of the molecular reflections at the surfaces that are in relative motion. The phenomena may be described conveniently by the introduction of the term "coefficient of slip." Ordinarily the momentum transfer through the gas is given by $\eta(V/d)$ where η is the coefficient of viscosity and V/d the velocity gradient. At low pressures the lessened momentum transfer may be written $\eta V/(d+2\zeta)$ where ζ is called the coefficient of slip in agreement with the hydrodynamical theory for the case of a flowing liquid slipping at a wall.

Maxwell[1] deduced from the kinetic theory the following value for ζ

$$\zeta = \frac{2-f}{f} \cdot \frac{\eta}{p} \cdot \sqrt{\frac{\pi RT}{2M}}$$

The fraction $(1-f)$ represents that portion of the impinging molecules reflected without any momentum transfer, or "specularly" reflected.

Stacy[2] and later Van Dyke,[3] using the constant deflection method for the determination of the coefficient of slip, found that f depended upon the nature of the surface. For a machined brass or old shellac surface, using air or carbon dioxide, no specular reflection was found. For oil and fresh shellac surfaces, specular reflection ranged from 8 to 21 per cent, and was greater for carbon dioxide than for air.

Some doubt might be cast on the precision of deductions from Maxwell's equation, since Maxwell himself remarks on the inaccuracy of his assumptions and suggests that the surface conditions arrived at in this way are liable to important corrections. The subject has also been treated by Baule.[4] His theory leads in a first approximation to an equation for the slip coefficient of the same form as Maxwell's. The fraction f is interpreted in terms of a coefficient which gives the fraction of the molecules that make only one collision with the surface, while the remainder make sufficient collisions to come into equilibrium with it. His formula becomes identical with Maxwell's in case $f=1$. Thus in both Maxwell's and Baule's theories arbitrary assumptions are made and no idea may be reached as to the degree of approximation attained in the formulas deduced.

The present investigation was undertaken with a view of determining Maxwell's f for the gases hydrogen, helium, air and oxygen from the coefficient of slip, employing the constant deflection method. Further, the attempt was made to check the results obtained from the coefficient of slip by working at pressures so low that the mean free path is considerably greater than the distance between the cylinders. Under these conditions a very simple theory applies, as the momentum is directly transferred, and the number of impacts per cm^2 per second equals $\frac{1}{4}n\bar{c}$. The tangential force per cm^2 on the inside cylinder is, therefore, equal to $\frac{1}{4}n\bar{c}mV$, where m equals the mass of the molecule and V is the velocity imparted due to the motion of the outside cylinder. Should the results of both methods be in agreement, the use of Maxwell's formula would be

[1] Maxwell, Scientific Papers, Vol. II, p. 708
[2] Stacy, Phys. Rev. **21**, 239, 1923
[3] Van Dyke, Phys. Rev. **21**, 250, 1923
[4] Baule, Ann. der Phys. **44**, 145, 1914

justified for the purpose of making deductions as to the nature of the collisions at the walls.

To eliminate troubles formerly experienced due to the release of occluded gases from the walls and consequent contamination of the gas under investigation, the "constant flow" method was used. It was thought that by continuous circulation, the gas could be kept sufficiently pure at these low pressures to admit of reliable measurements.

Apparatus

The apparatus consisted of two concentric cylinders, the outer one rotated at a constant rate by a driving mechanism operated by a falling weight, the inner one suspended by a steel wire, the deflection being observed by a telescope and scale. Because of slight variations in the de-

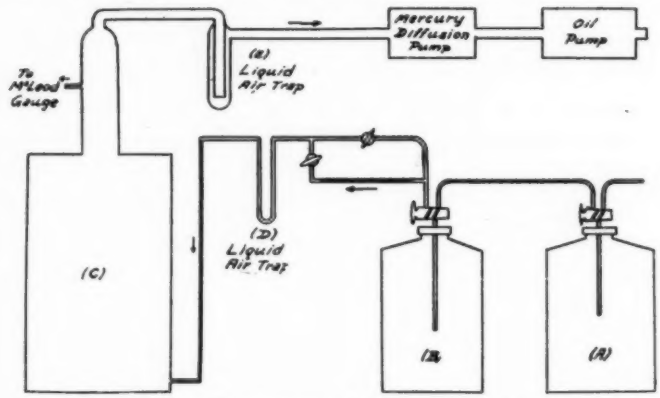


Fig. 1. Diagrammatic sketch of apparatus.

flection, scale readings were taken every half minute, the size of the drum upon which the chronograph record was made allowing about thirty such readings to be taken. The average of these was regarded as the deflection for the pressure recorded. The pressure in every case was a mean of four or five pressure readings taken during the run.

The brass surfaces were coated with a thin coat of silver oxide by rotating the cylinders in a silver nitrate solution. The silver deposited was immediately oxidized. This surface was later polished and made as smooth as mechanical means would permit. Before mounting, the surfaces were carefully cleaned with benzene, ether and alcohol. The details concerning the construction of the driving mechanism and cylinders are fully described by Gilchrist[5] in his paper on the viscosity of air.

The modifications and additions that were made so that continuous circulation of the gas would be possible are clearly shown in the dia-

[5] Gilchrist, Phys. Rev. 1, 124, 1913

grammatic sketch. The gas was pumped out of the apparatus by a mercury diffusion pump through a liquid air trap E. It was allowed to flow into the apparatus through a capillary and finally through liquid air trap D. It was found that the pressure in C could be kept very constant during the time that the run was being taken. To change the pressure to any desired value, it was only necessary to allow gas to flow into the reservoir B from the storage tank A.

The dimensions of the cylinders are as follows: Radius of outer cylinder 6.063 cm; radius of nner cylinder 5.341 cm; length of inner cylinder 24.88 cm; distance between cylinders .722 cm.

The scale was about 236 cm distant from the mirror on the suspension and deflections of 30 to 70 cm were obtained in the slip observations.

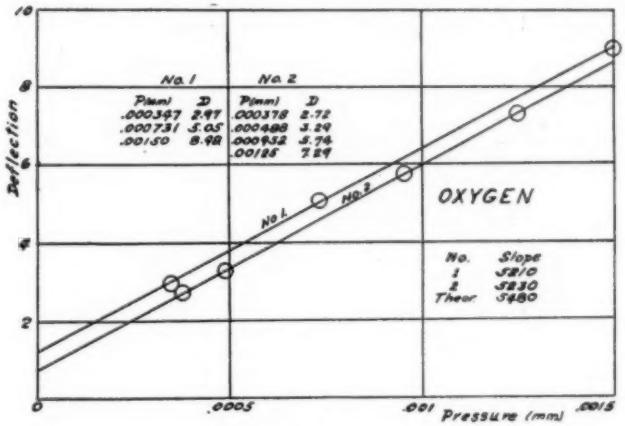


Fig. 2

While the slip observations were being made, the gas was allowed to circulate continuously through the apparatus.

The hydrogen gas was taken from a tank and allowed to pass through a long tube of heated copper filings for the purpose of removing any oxygen present, then through tubes of NaOH and P_2O_5.

The helium was also taken from a tank, and purified by passing through charcoal tubes kept at liquid air temperature. For slip determinations in helium, the apparatus was changed slightly in order to purify the gas more rapidly and also to save the gas. The outlet of the mercury diffusion pump was connected to the inlet of the helium reservoir and the same gas circulated continuously through the apparatus. In this way purification was effected very quickly, only a few minutes being required for all the air lines at first visible in the spectrum, to disappear.

Oxygen was prepared by heating potassium permanganate and was then allowed to flow through liquid air into the reservoir.

The air used was carefully dried by passing through phosphorous pentoxide and calcium chloride tubes.

All the gases were examined spectroscopically and found pure.

THEORY

(A) *Low pressure.* Kinetic theory gives that the number of impacts per cm² per sec. $=\frac{1}{4}n\bar{c}$. If the velocity of the outside cylinder is V, and a fraction f of the impinging molecules is diffusely reflected, the tangential force per cm² of the inside cylinder equals $\frac{1}{4}nm\bar{c}Vf=\frac{1}{4}\rho\bar{c}Vf$, where ρ is the gas density.

From kinetic theory it can also be shown that $\rho\bar{c}=2p\sqrt{(2M/\pi RT)}$.

We have, therefore, that the tangential force on the inside cylinder per cm² is $\frac{1}{2}\sqrt{(2M/\pi RT)}\cdot Vfp$ where M = molecular weight, R = gas constant, T = absolute temperature, and p = pressure.

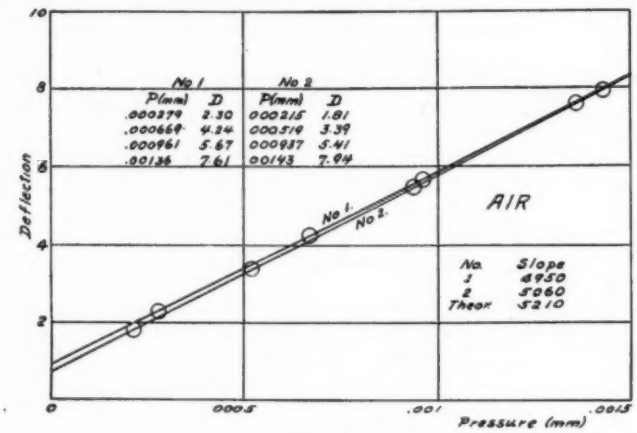


Fig. 3

At high pressures the tangential force per cm² $=\eta V/d$ where η is the coefficient of viscosity and d is the distance between the cylinders.

Since the deflection of the inner cylinder, d_p, is proportional to the force per cm², the constants of the apparatus can be eliminated if the force at low pressures is divided by the force at high pressure, and the ratio placed equal to the ratio of the deflections respectively.

We then obtain

$$\frac{d_p}{d_P}=\frac{f_p}{f_P}=\frac{d}{\eta}\sqrt{\frac{M}{2\pi RT}}\cdot fp=Kf$$

where $K=(d/\eta)p\sqrt{(M/2\pi RT)}$, a constant for a given gas at a fixed temperature. Since all observations are reduced to a common velocity, V does not enter in this formula. f, the quantity sought, is then equal to the ratio of the slope of the line found experimentally by plotting de-

flection against pressure, to K, which can be computed from well-known constants.

(B) *Slip determinations.* From the definitions in the first paragraph, it is seen that the deflection at low pressure is less in the ratio $(1+2\zeta/d)$. ζ is found to be inversely proportional to the pressure so that the coefficient of slip reduced to 76 cm pressure or $\zeta p/76$ may be calculated from the ratio of deflections at high and low pressures.

Further theoretical discussions on the determination of the slip coefficient are given in a recent paper by Professor Millikan.[6]

Observations

The coefficients of slip, reduced to 76 cm of mercury, are tabulated in Table I, with the corresponding pressures in the adjacent column. The average for each gas is compared with the value computed from Maxwell's formula, putting f equal to unity. For hydrogen and helium the experimental and theoretical values differ by less than one per cent, which is well within experimental error. For air and oxygen, the experimental value is about three per cent higher than the theoretical value, indicating a slight amount of specular reflection.

TABLE I

Coefficients of slip

Hydrogen		Helium		Air		Oxygen	
p (mm)	ζ_{760} (10^{-7})	p (mm)	ζ_{760} (10^{-7})	p (mm)	ζ_{760} (10^{-7})	p (mm)	ζ_{760} (10^{-7})
0.397	121	0.339	189	0.102	67.7	0.102	71.9
0.315	122	0.316	191	0.103	68.8	0.102	71.9
0.304	120	0.312	193	0.0918	68.2	0.103	72.6
0.270	118	0.314	192	0.125	68.9	0.0982	72.5
0.360	121	0.316	188	0.128	68.8	0.0921	72.3
0.305	122	0.397	188	—	—	0.0893	71.8
0.249	120	0.394	188	—	—	—	—
		0.390	193				
Aver.	121	—	190	—	68.5	—	72.1
Theor.*	121	—	191	—	66.2	—	70.2

All readings are reduced to 23°C and 760 mm pressure.
*Computed assuming $f=1$.

The results obtained at very low pressures are best shown graphically. Two graphs are given for each gas.

Figs. 2–5 in which the deflections are plotted against the pressure, clearly show the existence of a linear relation at these low pressures, and of a deflection intercept. At the low pressures, trouble was expected due to the presence of mercury vapor, since the rotating cylinder was operated

[6] Millikan, Phys. Rev. **21**, 217, 1923

from the outside through a mercury seal, although it was thought that the constant circulation of gas through liquid air would minimize the effects of mercury vapor.

In all cases the deflection at low pressures was a linear function of the pressure, but always indicated a deflection at zero pressure. Observations at higher pressure showed a gradual decrease in slope. This deflection intercept became smaller the longer the liquid air remained in contact with the apparatus, although the change after the liquid air had been on for about seventy-five hours was slight. Accompanying this decrease in intercept was an increase in slope. This intercept was no doubt due to vapors arising from stop-cock grease as well as to mercury vapor, and the longer the liquid air remained on the traps, the more vapor was condensed out. This slight increase in slope as the vapor disap-

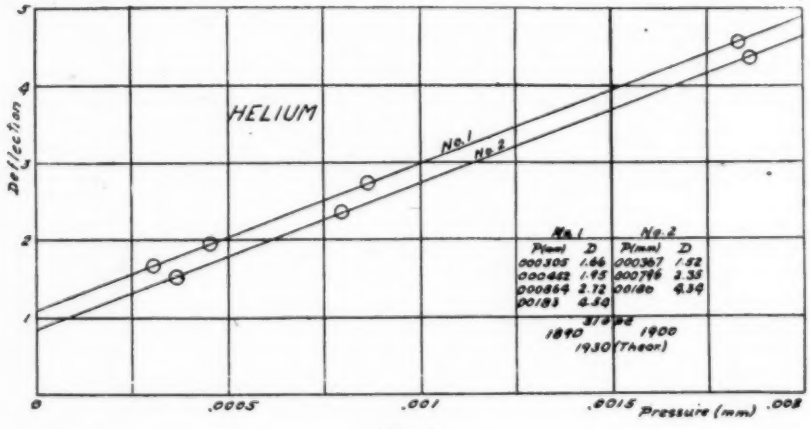


Fig. 4

peared is what wou'd be expected if the vapor is relatively more important at the lowest pressures read, due to a freer evaporation when the pressure is very low. Two or more curves are given for each gas to show the decrease of intercept and corresponding increase of slope as the liquid air remained longer in contact with the apparatus.

In each case the slope that was used for the computation of f was the slope of the curve having the smallest intercept and computed from data taken three days or more after the liquid air was put on.

For the gases hydrogen and helium specular reflection is entirely absent. Both investigations clearly indicate this. In oxygen and air, the two heavier gases, there seems to be a slight amount of specular reflection, possibly two or three per cent.

The values of f obtained from the slope at low pressures are slightly less than those obtained from the coefficient of slip, but this difference is

to be expected as the intercept of the line from which the slope was taken was not zero, and a further slight increase in slope, and therefore a slight increase in f would take place if the intercept were zero. Nevertheless,

TABLE II

Gas	*Maxwell's f* From slip	From slope
Hydrogen	1.00	0.99
Helium	1.00	0.99
Air	0.98	0.97
Oxygen	0.99	0.96

since the values obtained, as shown in Table II, agree to one per cent, it can be concluded that the results of both methods are in accord.

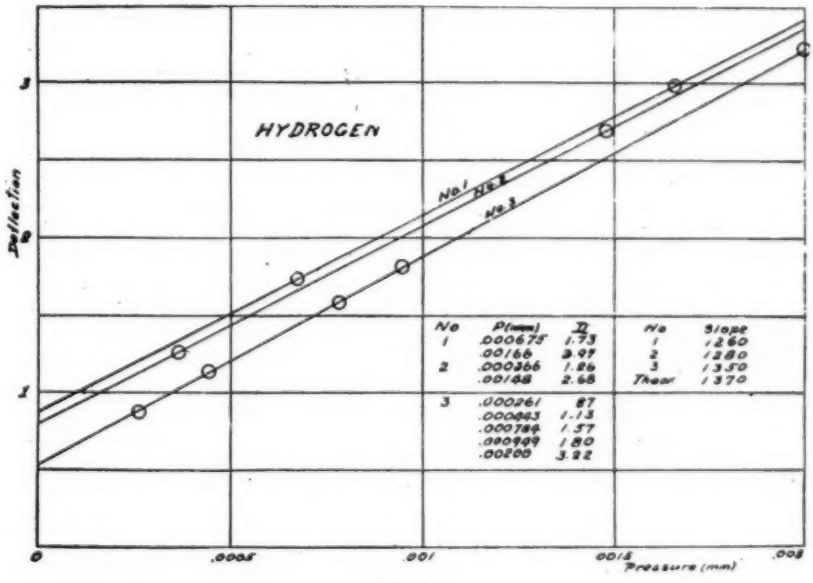


Fig. 5

This agreement between the two methods indicates that the deduction of diffuse reflection of the molecules at a wall from Maxwell's equation for slip is quite justifiable.

In conclusion I wish to express my indebtedness to Professor A. J. Dempster who suggested this investigation at low pressures, for the interest shown throughout this research, and for the ready help and advice he has accorded me. I wish also to thank Professor H. G. Gale and other members of the staff at Ryerson for helpful suggestions and interest shown.

RYERSON PHYSICAL LABORATORY,
June 15, 1923.

EXPERIMENTAL STUDY OF THE JOULE-THOMSON EFFECT IN CARBON DIOXIDE

By E. S. Burnett

Abstract

Joule-Thomson effect in carbon dioxide.—(1) *Experimental results for both vapor and liquid phases for 20 to 75 atm. and 0 to 120°C.* Dried CO_2, after compression to a high pressure controlled by a special regulator, was brought to a definite temperature, then adiabatically expanded radially inward through the walls of a porous porcelain tubular plug, successively to each of several lower pressures controlled by a second regulator. Pressures were measured with a modified Amagat differential free-piston manometer; the temperatures before and after passage through the plug were measured by Pt resistance thermometers. Since the expansion was adiabatic, the enthalpy, $g=(u+pv)$, was constant, and the observations secured, properly reduced, yielded *isenthalpic throttling curves* the slopes of which determine $\mu=(\partial t/\partial p)_g$, the Joule-Thomson coefficient. For both liquid and vapor phases μ is found to be a linear function of the isenthalpic temperatures and an exponential function of the isenthalpic pressures of such curves. In the liquid region μ becomes zero at -24°C for all pressures involved, and is negative at lower temperatures. The CO_2 used contained from 0.25 to 1.5 per cent air, but the author's results, obtained in 1910, are consistent with those of Jenkin and Pye (1914, 1915) which extended down to 10 atm. and to -55°C and were obtained with purer CO_2; also with those of Kester, and of Joule and Thomson, where comparable. (2) *Empirical formulas.* The entire experimental field for both phases, including the transition region in the vicinity of the critical point and along the saturation curve, has been represented by an empirical formulation, necessarily rather complicated. Isenthalps, isotherms and isobars of t, p, and μ computed from these formulas for the range 0 to 100 atm. from the solid-liquid phase-boundary at about -55°C through the liquid field into the super-heated vapor field as far as $+150$°C are presented in tabular and graphical form. More complete details will be given in a Bulletin of the University of Wisconsin.

Vapor pressure of CO_2, $-20°$ to $+30°$ C.—Results obtained from the experimental isenthalpic curves are compared with those of others, and all show good agreement with Keyes' equation.

WHEN a fluid is caused to pass adiabatically through a restricted passage or a porous plug under such conditions that its kinetic energy of flow on either side of the plug is negligible, then

$$u_1+p_1v_1=u_2+p_2v_2, \text{ or } u+pv=\text{ a constant} \qquad (1)$$

in which u_1 and u_2 are the specific intrinsic energies, v_1 and v_2 are the corresponding specific volumes at the respective pressures p_1 and p_2 before and after passing through the plug. The function $(u+pv)$, here designated by g, is known as the *enthalpy* of the fluid.

In a constant enthalpy porous plug expansion changes in both temperature and volume usually accompany the pressure drop across the plug; the limiting ratio of the temperature change Δt to the pressure change Δp as the latter approaches zero is variously known as the Joule-Thomson effect, the Joule-Kelvin effect, or simply the porous plug effect. This ratio, here designated by μ, is analytically defined by the relation

$$\mu = (\partial t/\partial p)_\theta \tag{2}$$

The present paper contains an account of the experimental arrangements and procedure by which values of μ for CO_2 have been obtained over considerable ranges of pressure and temperature; a brief discussion of the writer's data, their subsequent treatment and combination with similar data from other sources for grouping into isenthalpic curves; a brief discussion of the considerations controlling the development of an algebraic formulation of μ over the field covered by the data; and a comparison with the results of previous attempts by others to determine these relations.

Experimental Apparatus

The writer's experimental results were obtained in 1910 by the use of the almost ideal conditions obtained with the "radial flow" porous plug then described by Burnett and Roebuck.[1] For a complete description of this apparatus and the experimental procedure the reader is referred to the detailed account of this work to be published soon as a Bulletin of the University of Wisconsin.

The carbon dioxide was circulated by a single-stage refrigerating machine compressor which limited the investigation to a pressure range extending from 20 or 25 atmospheres to 70 or 75 atmospheres. From the compressor the CO_2 was passed through calcined calcium chloride for removing any water vapor that it might carry; then through a special and sensitive high pressure regulator that usually kept the initial pressure of the CO_2 constant to within two or three tenths of an atmosphere at seventy atmospheres pressure. It was then delivered (see Fig. 1) to a heat interchanger wherein the high pressure fluid passed the return flow from the plug and was thereby brought to a temperature approximately that of the liquid bath surrounding the plug chamber at which it arrived after passing through about seventy feet of one-quarter inch copper tubing coiled within the bath. The kerosene oil of the bath was circulated by a propeller in the direction shown by the arrows. Variations of temperature of the air in the brass-walled air-

[1] Burnett and Roebuck, Phys. Rev. **30**, 529, 1910

chamber which also served to direct the flow of the bath liquid, resulted in pressure and volume variations of this confined air which were used to

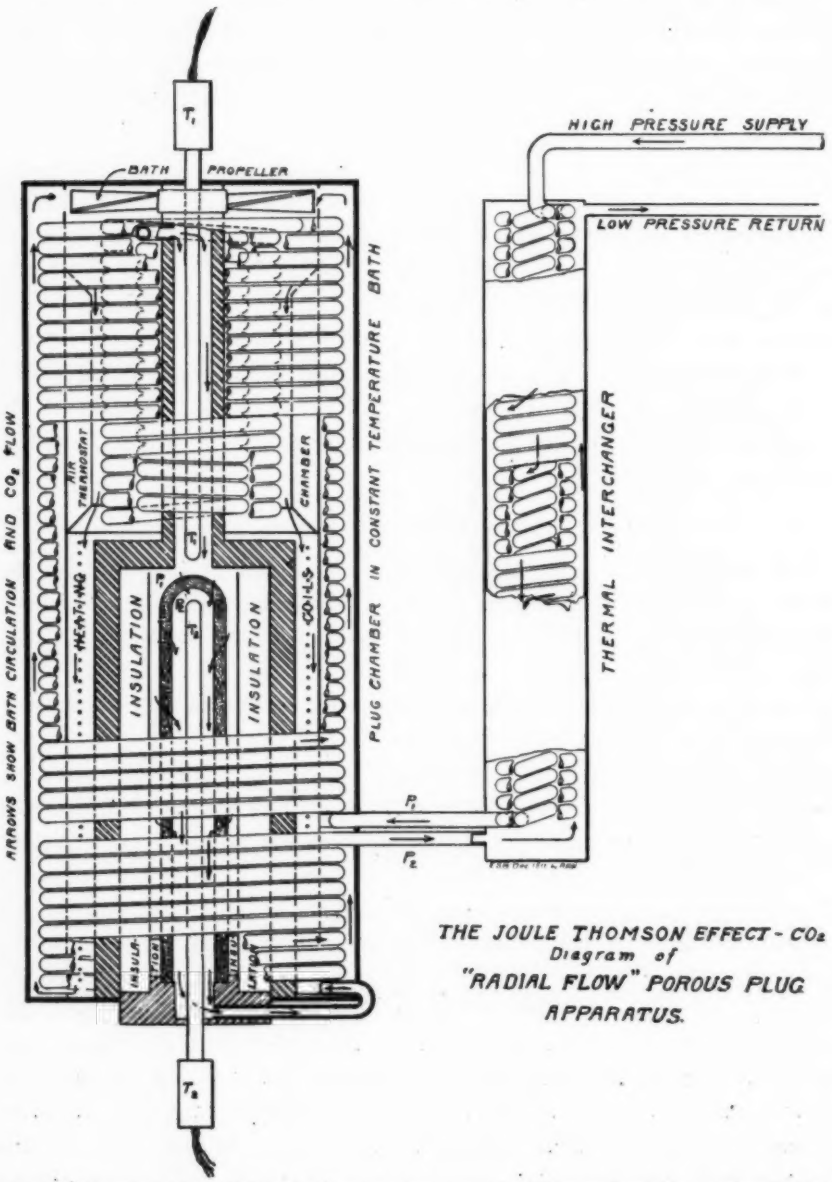


Fig. 1. Diagram of "radial flow" porous plug apparatus (approximately one-fourth size).

effect thermostatic control of the electric current applied to the heating coils located in the bath about the plug chamber.

The plug was of porous porcelain of the shape and proportions shown, copper plated at its open lower end and soldered to a steel block, details of which are not shown in the diagrammatic figure. The CO_2 then passed down along the outer plug surface within a slightly larger glass tube that was surrounded by a roll of asbestos paper which insulated the plug and glass tube from the walls of the plug chamber and also effectually prevented meandering of the CO_2 elsewhere than along the passage between the glass tube and the plug. It then diffused radially through the porous walls of the plug towards its inner surface, emerged at reduced pressure and temperature, and passed axially along the "low side" thermometer T_2; at the open base of the plug it was delivered to a short copper coil located in the lower part of the bath chamber and thence to the interchanger wherein it exchanged heat with the incoming high pressure CO_2; thence it proceeded through a low pressure regulator similar to the high pressure regulator above mentioned, and back to the compressor for re-compression and re-circulation.

Temperatures were measured, at the points shown, by two platinum resistance thermometers which could be used independently or differentially. The low side pressure was measured at the base of the plug, and the high side pressure was measured within the plug chamber outside of the plug. Pressures were measured with a modified form of the Amagat differential free-piston manometer[2] far more accurately than is possible with gauges of the Bourdon bent tube type.

Calibration of Apparatus

Resistance bridge and platinum resistance thermometers. Several calibrations of the binary scale resistances of the Callender and Griffiths' bridge by their method of substitution with the bridge wire were made during the course of these experiments. The fundamental intervals of the two platinum resistance thermometers were also checked several times during this period by comparison of their resistances at the ice and steam points; but because the range of temperature covered by these experiments was only from $-20°$ to $+120°$ C, no third point calibration was considered, since the makers (Cambridge Scientific Co.) had supplied the value 1.57 for the δ coefficient of the platinum wire of these thermometers.

From these data a table was prepared based upon the nominal values of the bridge box coils arranged in ascending series by steps of one box unit from -28 (bridge reversed) to $+128$, giving the corresponding

[2] E. H. Amagat, Ann. de Chimie et de Phys. (6), **29**, 1893; Harpers Scientific Memoirs, The Laws of Gases, p. 55.

centigrade temperatures for each thermometer after all box coil corrections, corrections for differences of fundamental intervals, and the δ correction were applied. Some slight variations shown by these calibrations are of small moment compared to variations in experimental results that appeared from other causes.

Differential free-piston manometer. Careful measurements of the essential dimensions of the free-piston manometer and of the relative displacements of the levels of the mercury in the mercury well and mercury column connected therewith, upon which the pressure measurements depended, taking into proper account the density of mercury at the latitude and elevation of the laboratory and at the mean temperature prevailing during the course of these experiments, gave the relation: change of pressure on free-piston manometer (in atmospheres) $=0.6495$ times the observed mercury column displacement.

Experimental Procedure

Having set the bath stirrer into operation and established a circulation of fluid from the compressor throughout the apparatus, the control pressures in the regulator receivers were set to give the desired initial high pressure and lowest final pressure. The thermostat and heating circuits were then adjusted to maintain the required initial temperature with the least possible variation. As soon as constancy of conditions had become established, observations were recorded in numbers sufficient to insure proper averages, after which conditions were changed and a new steady state sought.

Observations were recorded of resistances R_1, R_2 and R_Δ, respectively, of the high side thermometer T_1, the low side thermometer T_2, and of these thermometers differentially connected so as to give their temperature difference T_Δ; also of the heights H_1 and H_2, of the mercury column when the high side pressure p_1 or the low side pressure p_2, respectively, was acting on the differential free-piston manometer. The time of each observation was noted; also the zero of the mercury column, its temperature and that of the bridge box, the number and nominal values of the bridge coils in use for each bridge setting, and other items as occasion demanded.

Thus series of observations were obtained corresponding to several different pressure drops across the plug from as nearly as possible the same initial high side condition. The next run would yield similar series from some different initial condition, preferably from the same high side pressure but with a different high side temperature. From these observations, when properly reduced and grouped, were obtained isenthalpic curves the slopes of which determine μ (see Fig. 2).

Sampling and analysis of the carbon dioxide. Samples of the CO_2 were drawn from the delivery or low pressure side of the plug and were analyzed in an Orsat gas analysis apparatus. The results indicated about 0.025 per cent by volume of CO in the original samples of CO_2 and a trace of hydrogen. The general conclusion from the several

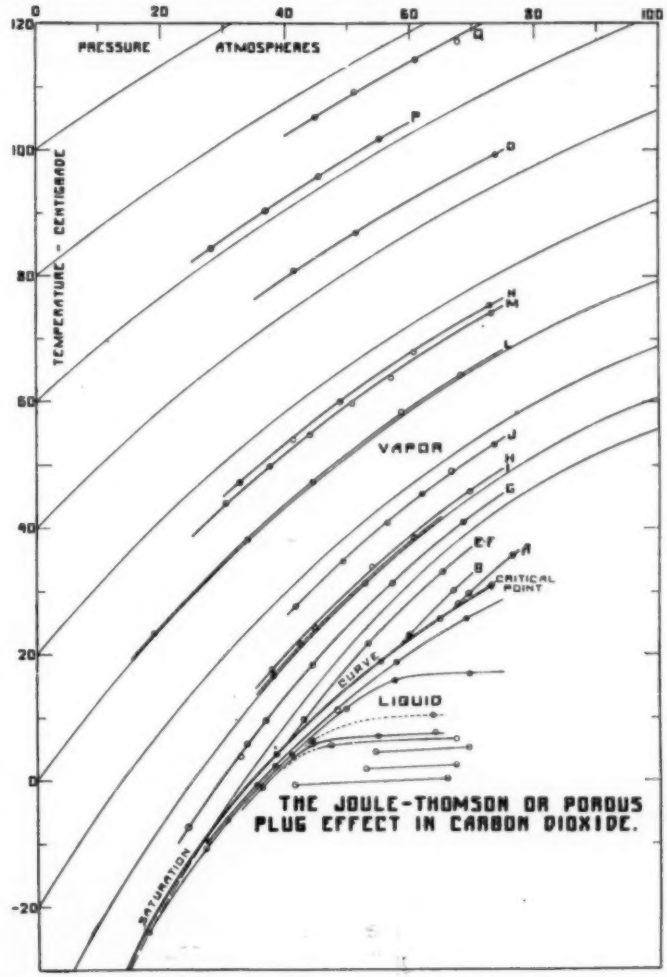


Fig. 2. Experimental isenthalpic or throttling curves; also curves computed from empirical formulation of 1913

analyses is that the volatile impurity found, which varied from about 0.25 per cent to 1.50 per cent by volume at atmospheric pressure, was mainly air in which the oxygen content was usually either normal or less than normal, ranging from 20 per cent down to 9 per cent, though one value of 24 per cent was obtained.

Reduction of the Observations

Sample set of observations. Table I shows a sample set of observations as recorded in the log book under the headings mentioned in a previous paragraph; the other items are self-explanatory; averages are also included. This table shows that the initial-temperature variations of this particular run were not serious; also, on the whole, the pressure variations of this run were not disturbing. A vertical comparison of the means under R_1 and H_1 shows but slight departures from a fixed initial condition.

Table II assembles the means selected to represent the observations sampled in Table I. It also gives the complete corrected values of temperatures, temperature differences, and pressures, in degrees centigrade and atmospheres, respectively, according to the calibrations; and it gives the average initial temperature and the average initial pressure for the whole run. Column headed (T_1-T_2) is added for comparison with the values of T_Δ; they should agree. Each line of Table II corresponds to the averages of one group of Table I and furnishes the data for one pair of points of an isenthalpic curve through the initial or high side point of the pair.

Adjustment to standard initial point. Deviations from the average for the run, of the initial points of the several pairs of points which serve to establish such a curve, imply corresponding deviations of greater or less magnitude of the low side points. An approximate corrective adjustment for these deviations is to shift the temperature and pressure of both points of a pair by amounts equal to the respective temperature and pressure deviations of its initial point from this average or standard initial point state. Table III shows the results of adjusting the data in this manner so that all low side points of a curve shall conform more closely to the isenthalp through a standard initial point. In columns 1 and 3 have been assembled the observed initial and low side temperatures, in columns 8 and 6 the observed initial and low side pressures, respectively, all transferred from Table II. T_1' and p_1' are the values selected as standard for the run. Column 2 gives $(T_1'-T_1)$, the temperature shifts, and column 7 gives $(p_1'-p_1)$, the pressure shifts to be added to columns 3 and 6 respectively to make their initial points approximately conform. The values of columns 4 and 5, the adjusted values, together with $(T_1'\ p_1')$, are the coordinates of the points plotted on the chart, Fig. 2, that are connected by the heavy-lined curve marked J; the other heavy-lined curves of this chart were similarly obtained from their corresponding observations.

The Experimental Isenthalpic Curves

A glance at Fig. 2 shows some of these curves intersecting the saturation curve for pure CO_2 near its upper end (see also Fig. 4). The observed values of pressure and temperature on the low side of the plug that fall below these intersections are distributed along the saturation curve but, to avoid confusion, are omitted from these charts. These relations show that if the porous plug expansion of CO_2 vapor starts from an initially superheated condition represented by any point near enough to the upper reaches of the saturation curve and be carried far enough, a part of the vapor will condense, so that the observed low side pressures and temperatures must be those of equilibrium between coexisting vapor and liquid phases. If the expansion be continued sufficiently far toward the region of low pressures the condensation of vapor will gradually decrease, re-evaporation of the condensate will ensue and eventually become complete; the isenthalp will emerge from the saturation curve at a certain low pressure and diverge therefrom toward the lower pressures and temperatures of the superheat field. This latter course of an isenthalp was not observed experimentally on account of the limitations set by the single-stage compressor available for this work; the charts do indicate however that such a course is undoubtedly the most likely one, and such a conclusion is supported by experimentally determined throttling curves for initially "wet" steam in the corresponding region of the steam field.[3] The charts show that there is one vapor isenthalp that just grazes the saturation curve at a point which it may be shown corresponds to that of maximum total heat of dry saturated CO_2 vapor.

The data for the liquid are much less satisfactory than are those for the vapor. It was much more difficult to control the experimental conditions when working with liquid CO_2; more initial point variation occurred, requiring larger and more uncertain adjustments to group the data into the curves shown in the liquid field of the chart, Fig. 2. The effect of impurities more volatile than the liquid is of considerable moment in this region. Each liquid isenthalp appears to merge gradually into a saturation curve of its own corresponding to the particular mixture represented by its components—CO_2 and air.

First formulation of experimental isenthalps. The light-lined curves of Fig. 2 spaced 20° apart on the temperature axis are computed from an empirical relation derived by 1913 in the course of early and un-

[3] See particularly the discussion and application of the throttling experiments on steam of Peake, Grindley, Griessman, and Dodge, by H. N. Davis, Proc. Am. Acad. Arts and Sci. **45**, 241–411, 1910.

successful attempts to formulate an expression that would represent the data over the entire experimental field. The equations given below do represent very satisfactorily, however, the experimental isenthalps of the vapor field that do not intersect the saturation curve and they were of great assistance in later applying more complete and proper adjustments to all of the original data which they cover. The equation of one of these curves is

$$t = t_0 + \mu_0 p + m p^n \tag{3}$$

in which t is the temperature centigrade at the pressure p atmospheres; μ_0 is the slope of the curve at its intercept (t_0, p_0) with the temperature axis; m and n are constants; m is negative and differs for each curve; n has a value greater than unity, taken as 5/3 for all curves covered. The several equations of this form are connected by the following relations between their coefficients, in which $T_0 = t_0 + 273$;

$$\mu_0 = 121{,}000/T_0^2 - 53/T_0; \qquad m = -3350/T_0^2 + 0.0155 \tag{4}$$

Later Treatment of Data

In the light of the studies outlined above, and of many others made then and since that are not detailed here, the original observations have been during 1922 once more subjected to the closest scrutiny. Some better average values have been obtained than those given in Table II. By the use of the 1913 empirical equations, supplemented where necessary, when possible, by graphical determination, these re-scrutinized original data have thus been better adjusted to conformity with fixed initial points than by the corrective approximation first used.

Correction for effect of air impurity in the CO_2. Practically the only direct evidence bearing on the effect of impurities such as air on the determination of μ for pure CO_2 vapor are the experiments of Kester[4] in 1905 and the original Joule and Thomson experiments on the cooling experienced by various mixtures of air and CO_2 when passed through a porous plug.[5] Kester's results in this regard are erratic and inconclusive. Joule and Thomson's values are also erratic but on the whole they show a definite variation of μ with a progressive variation of the components of their mixtures.

From a study of their data the writer was led to the conclusion that approximately one per cent of the observed temperature drops as corrected and adjusted in this later treatment of the data should be, and

[4] Kester, F. E., Phys. Rev. (1) **21**, 260, 1905

[5] Joule, J. P., and Wm. Thomson, Collected Papers (Thomson), I, p. 333, or Scientific Papers (Joule), II, p. 216; or Harper's Scientific Memoirs, Thermal Effects of Fluids in Motion, by Joule and Thomson.

therefore has been, added thereto for each one per cent of air content in the CO_2 vapor which he used. Since no definite knowledge of the impurity effect as a function of temperature and none at all of it as a function of pressure is available, no correction on the latter bases could be attempted. For similar reasons no attempt was made to apply proportional corrections to the temperature drops observed on passing liquid CO_2 through the plug.

Table IV presents in descending order of pressure and temperature magnitudes the finally acceptable values for all the runs, arranged in the order of the proximity of their graphs to the critical point. The

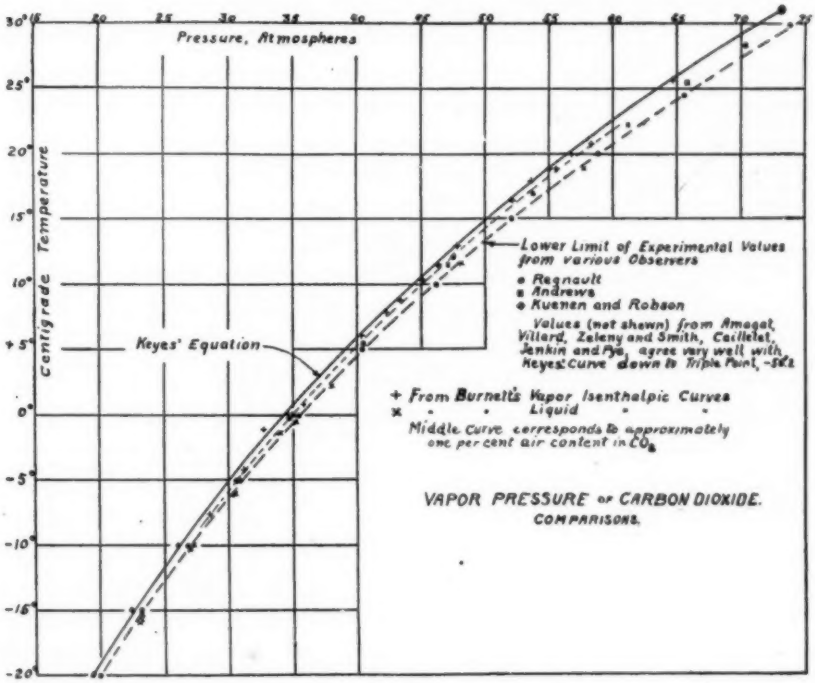

Pressure, Atmospheres
Centigrade Temperature
Keyes' Equation
Lower Limit of Experimental Values from various Observers
Regnault
Andrews
Kuenen and Robson
Values (not shown) from Amagat, Villard, Zeleny and Smith, Cailletet, Jenkin and Pye, agree very well with Keyes' Curve down to Triple Point, -56.2
+ From Burnett's Vapor Isenthalpic Curves
× " " Liquid " "
Middle Curve corresponds to approximately one per cent air content in CO2
VAPOR PRESSURE OF CARBON DIOXIDE.
COMPARISONS.

Fig. 3.

column headings are self-explanatory. The ± values were determined by comparison of $(T_1 - T_2)$ with T_Δ, which should agree. In the following Table V are grouped, on the basis of percentage of impurity, the uncorrected observed values of pressure and temperature for the experimental points that are found to lie along the saturation curve; these values are compared in Fig. 3 with the results of other observers; they are omitted from the chart, Fig. 4.

Table IV furnishes the values which are plotted as crosses (+) on the chart, Fig. 4. Of the writer's liquid curves shown thereon, the *first two points only* are plotted.

Throttling experiments of Jenkin and Pye. There are also shown on this chart, by circles (o) points corresponding to the throttling curves for CO_2 vapor and liquid from the experiments of Jenkin and Pye.[6]

The liquid "curves" of Jenkin and Pye are but two-point chords that extend much closer to the saturation curve than do the "first-two-point" chords of the writer's data. The volatile impurity (air) in their CO_2 was never more than 0.11 per cent by volume, about one tenth as much as was present in the CO_2 used by the writer. It appears most likely therefore that the trend of their liquid chords near the saturation curve is more nearly the trend for pure CO_2 than is that shown by the writer's liquid curves for his less pure CO_2 as represented on the chart, Fig. 2. The agreement of the slopes of the Jenkin and Pye liquid chords with those of the writer's "first-two-point" chords which are the more remote from the saturation curve where the effect of volatile impurity is much less, is further evidence that for pure CO_2 the trend of the liquid isenthalps approaching the saturation curve is of the order of that shown by Fig. 4 rather than of that shown by Fig. 2. Further developments herein are based upon that conclusion.

This close agreement of the values of Jenkin and Pye for liquid CO_2 as well as the close agreement of the general trend of the curves through their points for CO_2 vapor with that of the writer's curves in the vapor field, especially in the sections common to both, indicates that the two entirely independent sets of data are mutually concordant.

The experimental throttle-valve and other arrangements by which the observations of Jenkin and Pye were obtained are, in the opinion of the writer, inherently much more likely to introduce uncertainties in the accuracy of the observations than are those of the radial flow plug used by the writer. But in view of the concordance noted in these two sets of data as shown by the comparisons of Fig. 4 there appears to be no reason for assuming that either set is less reliable than the other; consequently from this point on both are used as a guide to the complete formulation from which the smooth curves of the chart, Fig. 4, and those following, have been computed.

The Complete Formulation

Choice of equation for isenthalps. The most direct method of attack is to select one form of equation between pressure and temperature to represent the course of each individual smooth curve drawn through the several points corresponding to each of the various runs represented

[6] Thermal Properties of Carbon Dioxide at Low Temperatures. Phil. Trans. A **213**, 67–118, 1914; A **214**, 353–382, 1915.

by the plots of Fig. 4, determine the coefficients of these several equations, and then find a cross relation between these coefficients and the temperature intercepts of their graphs on some constant pressure line such as $p=0$, $p=1$, $p=p_c$, the critical pressure, or p equal to some pressure greater than the critical pressure and therefore not involved with abrupt

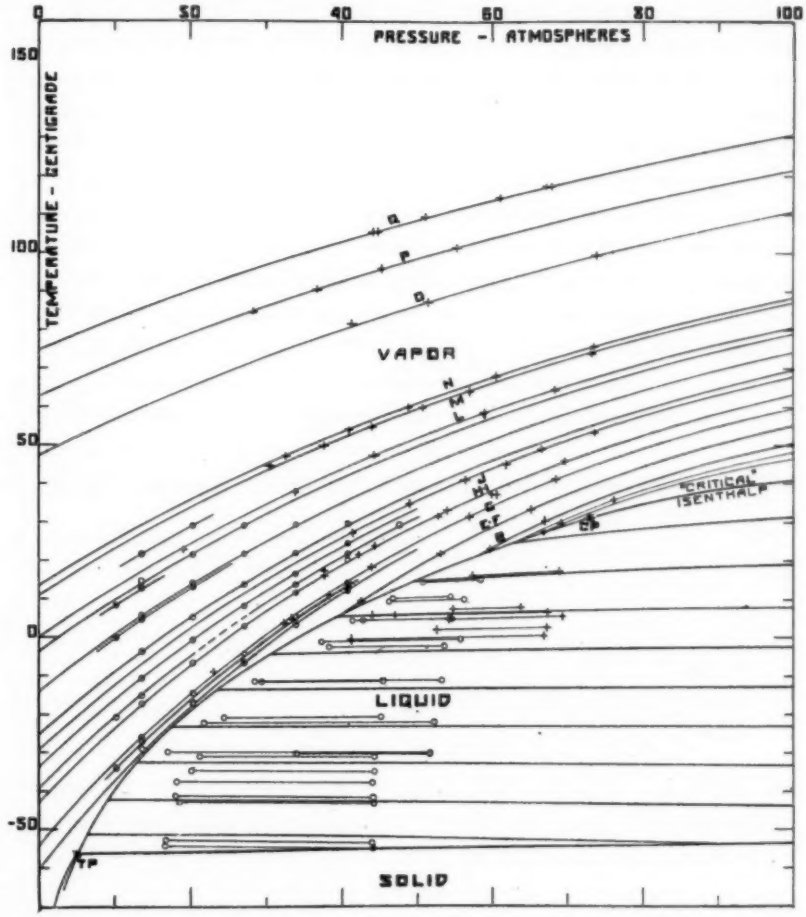


Fig. 4. Isenthalpic or throttling curves. Computed from an empirical formation by E. S. Burnett, 1922, based on data from experiments [+]. by Burnett in 1910, and from later independent experiments [o] by Jenkin and Pye in 1914-1915

phase changes. The critical pressure line was logically chosen as the reference pressure line since it is the first one in the direction of increasing pressures that is intercepted at any temperature (except at the critical point) by one and only one isenthalp.

It was found after considerable study that the various characteristic equations of state that have been proposed for fluids would not yield

expressions for isenthalpic curves or their derivatives that would satisfy the data. Effort was therefore concentrated on purely empirical forms of equations but with some regard to ease of modifying them to conform with additional data beyond the present experimental limits when such data be available.

Consideration was given to the probable courses of these curves when extended toward both higher and lower pressure limits; but in view of the absolute lack of any definite experimental controls for these external extensions the writer finally selected a form of equation for the isenthalps which continues undisturbed into the low pressure field their apparent trend as they approach from the higher pressure region, and which carries, in the direction of increasing pressures those isenthalps which cross the critical isobar above −24°C, and in the opposite direction those which cross it below that temperature, asymptotically toward finite temperature limits above which it seems likely that the true isenthalps will not rise.

The equation selected to represent each isenthalp is of an exponential form with two constants; it is obtained by integrating its derivative which expresses μ, the slope of the isenthalp, as a function of pressure, for it was observed that log μ, along an isenthalp, plots as a linear function of the corresponding pressure, whence,

$$\log (\mu/\mu')_\theta = b(p-p') \tag{5}$$

which is equivalent to

$$\mu = \mu' e^{b(p-p')} \tag{6}$$

in which μ' is the slope of the isenthalp at its intercept with the pressure line $p=p'$, and b is a parameter.

Putting $(\partial t/\partial p)_\theta$ for μ in Eq. (6) its integration yields

$$T-T' = (\mu'/b)[e^{b(p-p')}-1] \equiv (1/b)\ (\mu-\mu') \tag{7}$$

from which it is evident that along an isenthalp μ is by this equation represented as a linear function of the temperature as shown in Fig. 6, for on re-arranging Eq. (7) becomes

$$\mu = b\ (T-T')+\mu' \equiv bT+(\mu'-bT') \tag{8}$$

Also, solving Eq. (7) for p, we obtain

$$p-p' = \frac{1}{b}\log_e[\frac{b}{\mu'}(T-T')+1] \tag{9}$$

These several equations have a number of characteristics that make them particularly applicable to the limited data to which they are fitted; but the reader is referred to the complete account of this work to be published elsewhere[7] for an outline of these characteristics.

[7] Bulletin of The University of Wisconsin, Engineering Series, 1924

In expressing the relation found for μ' as a function of T' along the critical isobar $p'=p_c$, the critical pressure, the critical temperature and the slope $(dt/dp)_s$ of the saturation curve at the critical point, are all involved; the course of the saturation curve itself is also involved in locating the intersections of the isenthalps therewith. The values here used for these several quantities are taken from Keyes' formulations[8] based upon his consideration of data then available. They are:

$$p_c=72.9\text{ atm.};\ T_c=304.1^\circ\text{ K }(31.0^\circ\text{ C});\ \mu_c=(dt/dp_s)=0.6050^\circ\text{ C/atm.} \quad (10)$$

The last value, and the pressure-temperature values along the saturation curve, are from his equation,

$$\log_{10}p=12.0722-1496.7/T-2.8458\times10^{-2}T+3.64\times10^{-5}T^2 \quad (11)$$

in which p is in atmospheres, and T is in centigrade degrees of the absolute temperature scale. Keyes' formulations are used because they are the only ones known to the writer which express in continuous though empirical assemblies, from the triple point (-56.2° C, 5.15 atm.), to the critical point, all of the saturation properties of CO_2.

The relation found to represent μ' as a function of the absolute temperature T' along the critical isobar is as follows:

$$\mu'=\mu_c\left\{e^{2.3026\,(T_c/T')^2[0.1700-0.0765\,(T'-T_c)^{3/13}](T'-T_c)^{1/3}}\right\}-[(T'-T_c)/T']^{52/15} \quad (12)$$

in which the values are as previously defined.

This expression makes μ' zero at $T'=249.1^\circ$ K (-24.0° C); also at about 1642° K, far beyond these experimental limits, but near the point where we have some reason for expecting to find an inversion temperature for the sign of μ. Between these two temperatures μ' is positive, and has a maximum value of 0.7635 deg. per atm. slightly above the critical temperature at about 307.1° K; elsewhere μ' is negative; its rate of change with temperature is infinite at the critical point; nowhere is its rate of change zero except as infinitely high temperatures are approached, which is without significance here.

Formulation of b as a function of T'. The relation between b and T' which was found to satisfy certain arbitrary requirements as well as the "normal" ones expressed in equations (5) to (9) is given in the following equation

$$b=b_c\left(\frac{T'}{T_c}\right)^5 e^{-0.37\,(T'-T_c)^{\frac{1}{3}}}+0.0337\left[\frac{T'-T_c}{T'}\right]^{96/49} \quad (13)$$

in which $b_c=-0.04267$, $T_c=304.1^\circ$ K, and T' has the values previously defined.

[8] Keyes, F. G., and A. W. Kenney, Thermodynamic Properties of Carbon Dioxide, Am. Soc. Refr. Eng. Journ. **3**, 17–43, 1917.

One intended consequence of these relations is that all of the isenthalpic curves of the vapor field which intersect the saturation curve at all, shall do so twice, entering at a higher pressure and leaving at a lower pressure when viewed in the latter direction. The "critical" isenthalp enters at the critical point and leaves at the null point. Thus the vapor field is entirely covered by all of the curves above the critical isenthalp, and the liquid field by all of those below it.

At $T'=249.1°$ K ($-24.0°$ C) the isenthalp is a line of constant temperature—the inversion temperature of the liquid field, for which μ is zero at all pressures of the chart, Fig. 4, since the data are insufficient to disclose a variation of the inversion temperature with pressure. Below this temperature the liquid isenthalps have negative slopes, and eventually meet in the direction of increasing pressures, their limits at the liquid-solid phase-boundary[9] which crosses the field from the triple point [$p=5.15$ atm., $T=216.9°$ K ($-56.2°$ C)] through the point [$p'=72.9$ atm., $T'=218.5°$ K].

Table VI presents values of μ' and b computed from equations (12) and (13) as functions of T'. Values of $(db/dT')/b$ and $(d\mu'/dT')/\mu'$ as functions of T' are also given since they are of value for future operations. Most of the values given in Table VI were computed by use of six place logarithms, and are given to four or five significant figures for the sake of securing smoothness in the progressive variations of other magnitudes computed therefrom. A few were read from a large scale plot of the others.

The complete general equations for the whole field involved are of course obtained by combining equations (12) and (13) with equations (5) to (9), which combination yields admittedly cumbersome and unwieldy expressions that also involve transcendental relations. It is a matter of regret that the writer was unable to establish a simpler and more easily usable formulation. Every effort was made to obtain simplicity but the data cannot be simply represented.

Corresponding values of T, p and μ have been computed from this formulation for isenthalps spaced 10° or less apart on the critical pressure line and are presented in Table VII. Most of the computed values in this table were obtained by use of a circular slide-rule accurate to four significant figures and are so given for the reasons stated above. The isenthalps themselves are shown on the chart Fig. 5.

In Fig. 6 the curves depict μ as an *isobaric* function of temperature, and the straight lines as an *isenthalpic* function of temperature, both sets of loci being plotted from the values presented in Table VII. Values

[9] Tammann, Kristallisiern und Schmelzen, A. J. Barth, Leipsig, 1903, p 296

of μ as an *isothermal* function of pressure, obtained by cross-reading a large-scale plot of Fig. 6, are presented in Table VIII and Fig. 7.

Inspection of these several charts reveals at once that the relations disclosed are not simple. Attention is called to the reversion of the order of the curves of Fig. 6 at pressures up to 60 atm. between about 275° and 300° K (from 0° to 25° C). It is in this particular region that much of the work of previous investigators was done, and it is

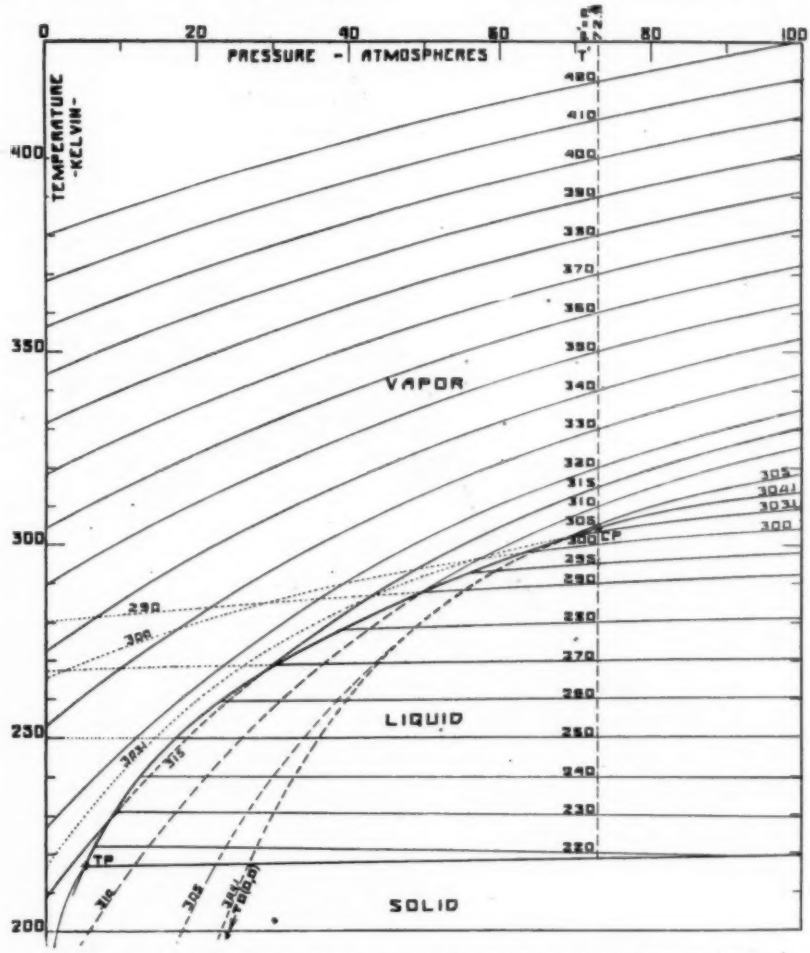
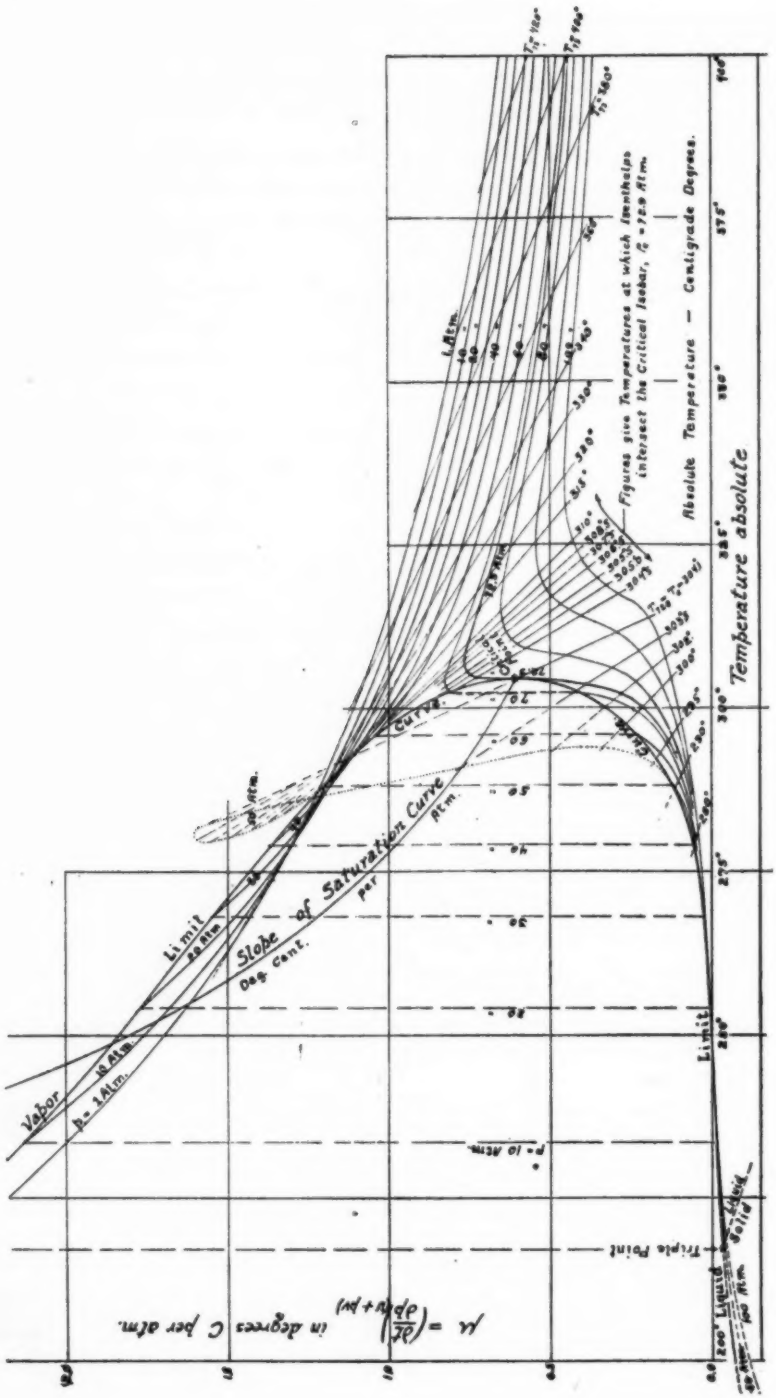


Fig. 5. Isenthalpic curves computed according to latest formulation

evident that here even slight variations in experimental results might lead to entirely discordant conclusions as to the character or magnitude of the true variation of Joule-Thomson effect, so that the discrepancies noted between the results of Joule and Thomson, Natanson, and Kester are not surprising.


Temperature absolute
Absolute Temperature — Centigrade Degrees.
Figures give Temperatures at which Isenthalps intersect the Critical Isobar, P = 72.9 Atm.
Slope of Saturation Curve
Limit
Vapor
Triple Point
Solid
Liquid
Curve
Limit
Curve
Limit
Limit
Limit

Comparison of Various Results

Fig. 8 furnishes some comparisons of the results of these previous investigators with the results from the present formulations which are based upon the experimental observations of the writer combined with those of Jenkin and Pye.[6] On the temperature basis of comparison, Kester's[4] values of μ are considerably higher than those of Joule and

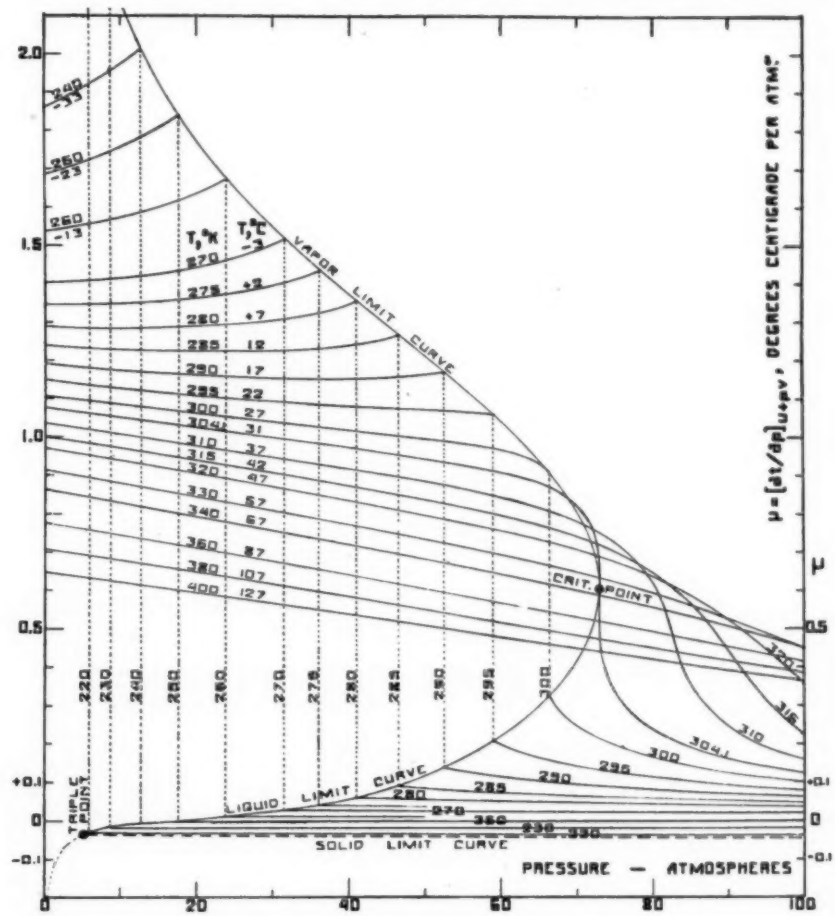


Fig. 7. Isothermal variation of μ with pressure

Thomson;[5] these are all for low pressures up to 15 atm. The writer's extrapolated values for 1 atm. and 10 atm. are seen to fall about midway between those of Kester and those of Joule and Thomson, but to favor the latter at the lower temperatures and the former slightly at the higher temperatures. None of their values was used by the writer as a guide in his formulation, so that it is reassuring that the rather wide

extrapolation over some 10 atm. at the lower temperatures of this comparison to some 40 atm. at the higher temperatures, yields values consistent with the only previously determined values of other investigators that are available for comparison.

Fig. 8 also shows some comparisons of the variation of μ with pressure at constant temperature. Natanson's[10] and Kester's results, where

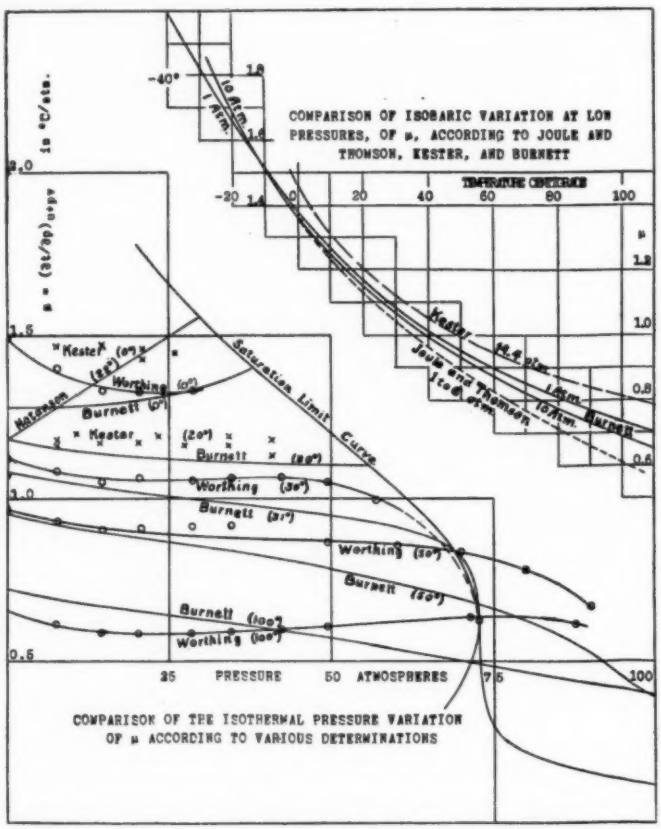


Fig. 8

comparable, are either mutually discordant or indeterminate. Worthing[11] computed μ from its thermodynamic relations to other known or assumed data on the properties of CO_2 including his own experimental determination of the ratio of its constant pressure and constant volume specific heats. His isotherms of μ thus determined show in some sections of the field a striking similarity of form to those of the writer, although the

[10] Natanson, Wied. Ann. **31**, 502, 1887
[11] Worthing, Phys. Rev. **33**, 256, 1911

agreement as to location throughout their courses is not so good. His computations, however, involve considerable uncertainty in some of the data used as well as some small difference factors between large and somewhat uncertain quantities. The comparison is of interest chiefly because of the similarity of form which it discloses.

Other comparisons are made in the detailed account of the development of the writer's present formulation, to which reference has been made[7] which further tend to support confidence in the belief that this formulation, besides representing within the limits of experimental uncertainty the facts disclosed by the data over their actual range, does also indicate with a close approximation to the probable truth the pressure and temperature variation of the Joule-Thomson effect in CO_2 over the extended range of these charts which is from zero to 100 atmospheres in pressure range, and from under 200° to over 400° in range of absolute temperature (°K).

By means of this formulation the variation along the isenthalps of the specific heat at constant pressure has been determined, and, by combination with absolute values of specific heats and other data for CO_2 determined from other sources, charts and tables have been prepared showing the variation of specific heat at constant pressure as a function of pressure and temperature, and also the variation of the heat-content of CO_2 liquid and vapor with pressure and temperature. Discussion of these and additional developments will be presented in subsequent papers.

The experimental work leading up to and including that herein described was conducted by the writer at the University of Wisconsin under the joint auspices of the College of Engineering and the Department of Physics of the University during the years 1905-1910; it was financed by University funds, assisted toward the end of that period by grants from the Count Rumford Research Fund.

MADISON, WISCONSIN,
April 21, 1923.

TABLE I

SAMPLE SET OF OBSERVATIONS

Resistances are expressed in bridge box units; pressures in cm of Hg

Date: Wed. P. M., Aug. 17, 1910. *Zero of manometer column, +1.50 cm*

Time	R_1	Time	R_2	Time	R_Δ	Time	H_1	Time	H_2
2:51	53.08	2:56	28.19	2:58	24.83	2.56	113.04	2:54	63.54
3:01	53.12	3:03	28.24	3:04	24.84	3:00	113.04	3:06	63.65
3:06	53.11	3:08	28.40	3:09	24.95	3:08	113.06	3:12	63.80
3:10	53.11	3:12	28.39	3:13	24.91	3:15	113.05	3:18	63.84
3:15	53.15	3:17	28.39	3:18	24.75	3:23	113.05	3:21	63.86
3:21	53.15	3:22	28.43	3:24	24.75	3:24	113.04	3:27	63.90
3:25	53.13	3:27	28.45	3:29	24.68	3:29	113.08	3:30	63.90
Means	53.12		28.36		24.82		113.05		63.78
3:38	53.17	3:42	35.57	3:44	17.57	3:38	113.05	3:43	75.58
3:45	53.17	3:47	35.58	3:48	17.57	3:48	113.04	3:50	75.58
3:49	53.17	3:50	35.58	3:51	17.57	3:53	112.95	3:54	75.55
3:53	53.16	3:55	35.60	3:56	17.56	3:59	112.94	3:56	75.55
3:58	53.16	4:00	35.62	4:03	17.56	4:03	112.86	4:00	75.52
Means	53.17		35.59		17.57		112.97		75.56
4:08	53.18	4:12	41.82	4:14	11.36	4:13	113.05	4:11	86.70
4:16	53.17	4:17	41.82	4:18	11.36	4:19	113.05	4:17	86.70
4:19	53.17	4:20	41.82	4:22	11.36	4:22	113.05	4:23	86.70
Means	53.17		41.82		11.36		113.05		86.70
4:32	53.17	4:36	46.17	4:38	6.84	4:32	113.00	4:35	95.20
4:45	53.18	4:48	46.37	4:50	6.90	4:43	112.94	4:46	94.82
4:53	53.21	4:54	46.23	4:55	6.85	4:51	112.62	4:53	95.02
4:58	53.14	4:58	46.23	4:59	6.87	4:56	113.00	4:57	95.02
5:00	53.14	5:01	46.19	5:03	6.88	5:03	112.97	4:59	95.03
5:04	53.15	5:05	46.20	5:06	6.86	5:07	113.00	5:04	94.82
5:07	53.11	5:08	46.17	5:10	6.92	5:10	112.93	5:09	95.02
Means	53.17		46.22		6.87		112.89		94.99
5:22	53.10	5:25	49.84	5:27	3.29	5:23	113.10	5:26	102.40
5:28	53.15	5:29	49.84	5:30	3.29	5:28	113.06	5:30	102.35
5:33	53.16	5:34	49.84	5:35	3.29	5:35	113.05	5:36	102.28
5:36	53.16	5:37	49.84	5:38	3.29	5:38	113.05	5:40	102.22
5:40	53.16	5:41	49.84	5:42	3.30				
Means	53.14		49.84		3.29		113.06		102.33

Temperature of box varied from 26.6° to 27.25°; temperature of mercury column from 29.0° to 29.5°.

TABLE II

MEAN VALUES FROM TABLE I

Temperatures in degrees C; pressures in atmospheres

R_1	T_1	R_2	T_2	R_Δ	T_Δ	T_1-T_2	H_1	p_1	H_2	p_2	p_1-p_2
53.12	53.26	28.36	27.47	24.82	25.75	25.79	113.05	73.48	63.78	41.46	32.02
53.17	53.31	35.59	34.80	17.57	18.16	18.51	112.97	73.43	75.56	49.12	24.31
53.17	53.31	41.82	40.93	11.36	12.42	12.38	113.05	73.48	86.70	56.35	17.13
53.17	53.31	46.22	45.35	6.87	8.00	7.96	112.89	73.38	94.99	61.74	11.64
53.14	53.28	49.84	49.00	3.29	4.32	4.28	113.06	73.49	102.33	66.51	6.98
Means 53.29								73.45			

TABLE III

REDUCTION OF VALUES IN TABLE II TO $T_1' = 53.30$; $p_1' = 73.50$

Date: 8-17-'10 *Impurity*: 0.75 *per cent by volume, N T P.*

T_1	$T_1' - T_1$	T_2	T	p	p_2	$p_1' - p_1$	p_1
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
53.26	+0.04	27.47	27.51	41.48	41.46	+0.02	73.48
53.31	−0.01	34.80	34.79	49.19	49.12	+0.07	73.43
53.31	−0.01	40.93	40.92	56.37	56.35	+0.02	73.48
53.31	−0 01	45.35	45.34	61.86	61.74	+0.12	73.38
53.28	+0.02	49.00	49.02	66.52	66.51	+0.01	73.49

TABLE IV A

VAPOR ISENTHALPS; EXPERIMENTAL VALUES

Pressure in atmospheres; temperature in degrees centigrade

Curve	p	t		Curve	p	t		Curve	p	t	
A	76.10	35.70		B	66.90	30.20		C, D	68.60	33.20	
Aug. 17	69.14	29.72	±0.03	Sept. 17	59.78	23.02	±0.09	Aug. 18, 19	62.76	28.23	±0.05
	66.67	27.49	0.06		59.72	22.98	0.11		58.77	25.20	0.08
(impurity	64.54	25.51	0.01	(impurity,	saturation			(impurity,	55.74	22.15	0.06
1.05%)	saturation			0.060%)	56.68	20.00	0.01	1.12%)	46.68	12.34	0.12
	64.54	25.54	0.01		55.08	18.77	0.05		saturation		
	58.34	20.66	0.02		52.08	16.28	0.06		40.31	+6.00	0.38
	47.56	11.91	0.14		47.86	12.84	0.10		35.80	+0.80	0.25
	34.67	−0.42	0.17		46.33	11.39	0.06		32.76	−1.16	0.34
					45.02	10.23	0.10		31.22	−4.28	0.17
					42.28	7.73	0.05				
E	65.10	33.10		F	61.00	32.95		G	68.40	41.00	
Sept. 14	53.12	21.70	±0.10	Sept. 14	34.25	3.63	±0.16	Sept. 15	56.82	31.28	±0.01
	42.60	9.58	0.13	(impurity,					43.98	18.30	0.04
(impurity,	saturation			1.25%)				(impurity,	38.31	10.98	0.06
1.25%)	34.60	0.00	0.16					0.50%)	33.41	+4.81	0.15
	28.48	−7.40	0.19						32.39	+3.69	0.13
									23.11	−9.04	0.21
H	60.50	37.00		I	69.60	45.90		J	73.50	53.30	
Aug. 21	52.66	31.17	±0.03	Aug. 12	53.90	32.95	±0.02	Aug. 17	66.52	48.94	±0.02
(impurity,	42.25	21.45	0.05	(impurity,	44.44	23.86	0.07	(impurity,	61.74	44.89	0.06
1.06%)	37.71	16.09	0.13	1.06%)	37.66	17.28	0.07	1.14%)	56.35	40.73	0.02
									49.11	34.68	0.17
									41.46	27.18	0.03
L	68.20	64.30		M	73.10	73.60		N	73.40	75.40	
Sept. 16	58.87	58.34	±0.04	Aug. 16	56.89	64.02	±0.04	Aug. 27	60.42	67.91	±0.04
(impurity,	44.32	47.20	0.04	(impurity,	50.59	59.58	0.02	(impurity	48.91	59.65	0.15
0.83%)	33.87	37.86	0.05	1.25%)	43.96	54.73	0.04	0.97%)	40.92	54.08	0.07
	19.09	22.90	0.05		37.62	49.59	0.04		32.51	47.06	0.02
					30.47	44.62	0.05				
O	73.80	99.30		P	55.10	101.20		Q	67.70	117.30	
Aug. 27	51.43	87.05	±0.12	Sept. 29	45.25	95.79	±0.00	Sept. 23, 24	61.00	114.32	±0.06
(impurity,	41.36	81.54	0.12	(impurity,	36.69	90.35	0.05	(impurity,	51.06	109.22	0.03
1.50%)				0.90%)	28.36	84.69	0.17	0.90%)	44.78	105.28	0.14

TABLE IV B

LIQUID ISENTHALPS; EXPERIMENTAL VALUES

Pressure in atmospheres; temperature in degrees centigrade

Curve	Percent impurity	Adjusted values p	t	Observed values, unadjusted p_1	t_1	p_2	t_2
a	0.30			71.92	31.25	55.53	18.77 ± 0.14
Sept. 18				72.22	31.22	53.68	17.83 0.59
				72.22	30.38	43.38	8.65 0.19
b	1.08	68.90	25.70				
Aug. 19		57.65	18.79 ± 0.04	68.92	25.65	57.65	18.73 ± 0.04
combined		48.90	11.12 0.08	68.84	26.07	48.09	11.52 0.08
with		38.00	+ 2.41 0.11	67.68	24.80	38.00	+ 2.23 0.11
Sept. 18		35.09	− 0.72 0.15	69.26	26.16	35.09	− 0.54 0.15
		27.25	− 9.65 0.30	69.72	25.70	27.25	−10.06 0.30
c	0.90	69.30	17.00				
Sept. 25		57.32	15.09 ± 0.00	68.93	17.09	57.32	15.97 ± 0.00
		49.55	11.35 0.08	68.96	17.09	49.55	11.37 0.08
		40.69	+ 4.16 0.14	69.62	16.99	40.69	+ 4.16 0.14
		30.38	− 6.27	68.83	16.41	30.38	− 6.22
		26.97	−10.66 0.26	69.22	14.64	26.97	−10.78 0.26
		17.63	−24.17 0.17	70.02	15.94	17.63	−24.21 0.17
d	0.50	Sept. 19		56.30	11.70	34.00	− 1.35 ± 0.02
e	0.80	Sept. 23		63.50	11.40	44.10	+ 6.45 0.20
f	0.85	63.80	7.75				
Sept. 23		54.77	7.10 ± 0.05	63.84	7.87	54.77	+ 7.26 ± 0.05
		44.03	+ 5.93 0.12	63.73	7.69	44.03	+ 5.84 0.12
		35.94	− 1.10 0.02	63.81	7.75	35.94	− 1.10 0.02
		23.21	−15.30 0.86	63.82	7.74	23.21	−15.30 0.86
g	0.4 to 0.2			67.30	6.70	47.10	5.60 ± 0.03
Sept. 23				69.35	5.40	54.25	4.60 0.04
				67.20	2.55	52.60	+ 1.90 0.07
				66.80	+0.25	41.25	− 0.70 0.03
				62.35	−0.20	23.05	−15.95 0.10
				65.25	−0.40	31.55	− 5.70 0.03
				61.45	−0.90	23.25	−15.80 0.21

TABLE V

SATURATION VALUES; EXPERIMENTAL

Average Impurity	Pressure atm.	Temperature degrees C
1.11%	65.54	25.55 ± .01
	58.34	20.68 .02
	57.65	18.79 .04
	48.90	11.12 .08
	47.56	12.05 .14
	46.68	12.78 .05
	40.31	6.00 .38
	38.00	+ 2.41 .11
	35.80	+ 0.80 .25
	35.09	− 0.72 .15
	34.67	− 0.25 .17
	34.60	0.0 .16
	32.76	− 1.16 .34
	31.22	− 4.28 .17
	28.48	− 7.67 .19
	27.25	− 9.65 .30

TABLE V—Continued

Average Impurity	Pressure atm.	Temperature degree C
0.87%	44.08	6.46 ± .20
	40.69	+ 4.16 .14
	35.94	− 1.10 .02
	30.38	− 6.22
	26.97	−10.78 .26
	23.21	−15.30 .86
	17.63	−24.21 .17
0.60%	56.68	20.00 ± .01
	55.08	18.77 .05
	52.08	16.28 .06
	47.86	12.84 .10
	46.33	11.39 .06
	45.02	10.23 .11
	42.28	7.73 .05
	34.00	− 1.35 .02
0.30%	55.53	18.77 .14
	53.68	17.83 .59
	43.38	8.65 .10

TABLE VI

VALUES DERIVED FROM EQS. (12 AND 13)

$T'_{(p=p_c)}$	μ'	$\frac{1}{\mu'}\left(\frac{d\mu'}{dT'}\right)$	b	$\frac{1}{b}\left(\frac{db}{dT'}\right)$
200°K	−0.10394	−0.05070	+0.009137	−0.02958
210	−0.06174	−0.05365	+0.006580	−0.03436
220	−0.03528	−0.05626	+0.004527	−0.04126
230	−0.01867	−0.06956	+0.002803	−0.05700
240	−0.007736	−0.11568	−0.001291	−0.11190
245	−0.003376	−0.24875	+0.000578	−0.24540
250	+0.000730	+1.1279	−0.000131	+1.0895
255	+0.004969	+0.17832	−0.000855	+0.17316
260	+0.009732	+0.10630	−0.001630	+0.09709
265	+0.01548	+0.08306	−0.002456	+0.07196
270	+0.02278	+0.07266	−0.003401	+0.05997
280	+0.04543	+0.06720	−0.005887	+0.05229
290	+0.09091	+0.07220	−0.010152	+0.05682
295	+0.13243	+0.08171	−0.013658	+0.06567
300	+0.021266	+0.11453	−0.019944	+0.09175
302	+0.27742	+0.15868	−0.02464	+0.12542
303.5	+0.3804	+0.31550	−0.03156	+0.23482
303.8	+0.4265		−0.03419	
304.1	0.6050	+∞	−0.04267	±∞
304.2	0.6922	+0.44701	−0.03742	−0.57456
304.3	0.7081	+0.25817	−0.03572	−0.38557
304.5	0.7264	+0.07519	−0.03357	−0.25718
305	0.7468		−0.03045	
305.5	0.7560	+0.16857	−0.02841	−0.12005
306.5	0.7628	+0.003387	−0.025614	−0.08480
307.5	0.7630	−0.000646	−0.02385	−0.06694
308.5	0.7603	−0.004870	−0.02243	−0.05596
310	0.7533	−0.007072	−0.020792	−0.04559
315	0.7223	−0.009074	−0.017458	−0.028334
320	0.6900	−0.009052	−0.015448	−0.020562
330	0.6331	−0.008696	−0.013108	−0.013190
340	0.5872	−0.006992	−0.011675	−0.009780
360	0.5200	−0.005252	−0.009982	−0.007630
380	0.4742	−0.004074	−0.008876	−0.005295
400	0.4410	−0.003241	−0.008042	−0.004632
420	0.4154	−0.002785	−0.007308	−0.004289

TABLE VII

ISENTHALPIC VALUES FROM 1922 FORMULATION

Pressures in atmospheres; temperatures in °K; μ in °K per atm.

p	0	1	20	40	60	72.9	80	100
				Vapor Isenthalps				
T	379.94	380.63	393.12	404.56	414.39	420.00	422.88	430.22
μ	0.7080	0.7029	0.6118	0.5284	0.4564	0.4154	0.3944	0.3407
T	356.30	357.10	370.92	383.40	394.00	400.00	403.05	410.74
μ	0.7924	0.7860	0.6748	0.5745	0.4892	0.4410	0.4165	0.3546
T	331.40	332.30	347.99	361.90	373.52	380.00	383.27	391.43
μ	0.9054	0.8974	0.6582	0.6348	0.5317	0.4742	0.4452	0.3728
T	304.30	305.35	323.77	339.76	352.85	360.00	363.57	372.35
μ	1.0760	1.0655	0.8816	0.7220	0.5914	0.5200	0.4844	0.3967
T	272.42	273.88	297.03	316.46	331.83	340.00	344.00	353.64
μ	1.3750	1.3590	1.0885	0.8620	0.6826	0.5872	0.5405	0.4280
T	226.91	229.09	263.56	290.42	310.15	320.00	324.63	335.27
μ	2.1272	2.0948	1.5620	1.1470	0.8422	0.6900	0.6184	0.4540
T	208.69	211.26	[252.26]	282.91	304.56	315.00	319.82	330.59
μ	2.5786	2.5338	[1.8181]	1.2826	0.9046	0.7223	0.6381	0.4501
T	181.28	[184.70	237.43	274.42]	298.85	310.00	314.97	325.60
μ	3.4295	[3.3588	2.2620	1.4928]	0.9850	0.7533	0.6500	0.4290
T	157.40	[161.24	226.49	269.35	295.97]	307.50	312.48	322.77
μ	4.343	[4.2514	2.6950	1.6727	1.0380]	0.7630	0.6442	0.3998
T	120.90	[126.80	212.44	264.32	293.71]	305.50	310.36	319.77
μ	6.000	[5.832	3.400	1.926	1.091]	0.7560	0.6179	0.3508
T	76.00	[81.40	198.40	260.85	292.77]	304.50	309.09	317.42
μ	8.396	[8.114	4.288	2.1915	1.1200]	0.7264	0.5724	0.2926
				Critical Isenthalp				
T	0.00	[13.38	182.77	260.56	293.70	304.10]	307.80	313.82
μ	13.580	[13.01	5.783	2.463	1.049	0.6050]	0.4470	0.1906
				Liquid Isenthalps				
T	[195.21	198.25	251.57	281.51	297.44]	303.50	305.92	310.43
μ	[3.7974	3.6800	2.0194	1.0744	0.5716]	0.3804	0.3041	0.1618
T	[245.42	247.07	271.83	287.94	297.79]	302.00	303.81	307.48
μ	[1.6720	1.6312	1.0210	0.6239	0.3812]	0.2774	0.2329	0.1423
T	[265.03	265.92	280.04	290.11	296.87]	300.00	301.41	304.45
μ	[0.9102	0.8924	0.6108	0.4099	0.2751]	0.2127	0.1846	0.1239
T	[275.86	275.93	277.16]	278.34	279.39	280.00	280.32	281.14
μ	[.06978	.06936	.06202]	.05514	.04901	.04543	.04357	.03873
T	[259.24	259.26	259.46]	259.67	259.88	260.00	260.07	260.26
μ	[.01096	.01094	.01064]	.01027	.00993	.00973	.00962	.00931
T	[240.54	240.53]	240.40	240.29	240.10	240.00	239.94	239.79
μ	[−.00704	−.00705]	−.00723	−.00742	−.00761	−.00773	−.00781	−.00801
T	[222.19	222.17]	221.66	221.08	220.44	220.00	219.74	218.98
μ	[−.02537	−.02548]	−.02778	−.03040	−.03329	−.03528	−.03464	−.03989

TABLE VII—Continued

Supplementary values at graphically determined intersections of the isenthalps with the saturation curve

T'	μ'	b	p_1	T_1	μ_1	p_2	T_2	μ_2	Remarks
315.85	0.7166	−0.01705	17.1	249.1	1.855	17.1	249.1	1.855	Tangent or grazing point
315.0			27.15	264.6	1.606	8.4	228.7	2.226	
313.88	0.7296	−0.01803	33.75	272.55	1.478	5.15	216.9	2.475	Lower point is triple point
312.75	0.7369	−0.01870	39.5	278.5	1.376	3.3	197.5	2.707	Lower point is on saturation curve extension below the triple point
310.0			50.45	288.35	1.2015				
307.5			59.3	295.25	1.0550				
305.5			66.5	300.15	0.9068				
304.5			70.7	302.75	0.7820				
304.1	**0.6050**	**−0.04267**	**72.9**	**304.1**	**0.6050**	**0.0**	**0.0**	**13.580**	Upper point is critical point, lower point is the null point (arbitrary)
303.5			69.9	302.3	0.4182				
302.0			66.3	300.0	0.3280				
300.0			62.6	297.5	0.2610				
280.0			39.25	278.25	0.0554				
260.0			23.5	259.5	0.0105				
249.1	0.0	0.0	17.1	249.1	0.0	Inversion temperature of the J-T effect for liquid carbon dioxide			
240.0			12.8	240.4	−0.0072				
220.0			6.5	222.0	−0.0261				
(214.1)	(−0.0496)	(+0.0568)	5.15	216.9	−0.03375	Triple point; (T', p') for this isenthalp is a point of solid phase			

NOTE: Values between brackets [] in the main part of this table indicate "mathematical" courses of the curves when both liquid and vapor phases are present; these are shown by the broken lined portions of a few of the curves of the chart Fig. 5. Physically and experimentally the temperatures and slopes observed are those of the saturation curve for the pressures corresponding to the values within the brackets.

TABLE VIII

Isothermal and isobaric values of μ corresponding to the charts of Figs. 6 and 7, expressed in deg. C per atm.

Temp. °K	Pressure in atmospheres 0	1	10	20	40	60	72.9	80	100
				Vapor phase above line					
400.0	0.6475	0.6440	0.6210	0.5950	0.5375	.4790	.4410	.4225	.3635
390.0	0.6755	0.6725	0.6485	0.6200	0.5595	.4965	.4560	.3850	.3235
380.0	0.7080	0.7045	0.6780	0.6475	0.5835	.5165	.4742	.4505	.3855
370.0	0.7415	0.7335	0.7100	0.6775	0.6160	.5405	.4952	.4705	.3995
360.0	0.7790	0.7750	0.7455	0.7110	0.6420	.5685	.5200	.4930	.4155
350.0	0.8195	0.8150	0.7850	0.7500	0.6780	.6020	.5500	.5210	.4340
340.0	0.8640	0.8595	0.8290	0.7950	0.7205	.5425	.5872	.5550	.4500
330.0	0.9140	0.9095	0.8795	0.8450	0.7720	.6925	.6331	.5945	.4490
325.0	0.9425	0.9375	0.9075	0.8745	0.8025	.7230	.6605	.6165	.4220
320.0	0.9710	0.9665	0.9380	0.9050	0.8360	.7570	.6900	.6380	.3570
315.0	1.0020	0.9985	0.9705	0.9395	0.8735	.7970	.7223	.6500	.2210
310.0	1.0360	1.0320	1.0055	0.9765	0.9160	.8435	.7554	.6100	.1585
305.0	1.0710	1.0675	1.0445	1.0155	0.9640	.9000	.7468	.2690	.1270
304.1	1.0775	1.0740	1.0505	1.0240	0.9735	.9100	.6050	.2420	.1215
300.0	1.1070	1.1045	1.0840	1.0600	1.0175	.9675	.2147	.1650	.1005
295.0	1.1480	1.1455	1.1270	1.1090	1.0805	.1990	.1324	.1134	.0794
290.0	1.1920	1.1900	1.1750	1.1635	1.1525	.1156	.9999	.0815	.0619
285.0	1.2395	1.2385	1.2280	1.2245	1.2400	.0761	.06355	.0586	.0478
280.0	1.2900	1.2900	1.2845	1.2915	1.3470	.0515	.0454	.0425	.0364
275.0	1.3455	1.3455	1.3470	1.3645	0.0414	.0355	.0324	.0309	.0275
270.0	1.4050	1.4060	1.4155	1.4455	0.0274	.0246	.0228	.0221	.0202
260.0	1.5375	1.5405	1.5735	1.6375	0.0106	.0101	.00973	.0096	.0090
250.0	1.6885	1.6954	1.7570	0.0°735	0.0°733	.0°731	.0°730	.0°729	.0°727
240.0	1.860	1.870	1.974	−0.00723	−0.00742	−.00761	−.00774	−.00781	−.00801
230.0	2.060	2.070	−0.0168	−0.0171	−0.0177	−.0183	−.0187	−.0190	−.0195
220.0	2.2855	2.3035	−0.0294	−0.0304	−0.0323	−.0341	−.0353	−.0359	−.0375
				Liquid phase below line					

Supplementary values at graphically determined intersections of isotherms and isobars of μ with the saturation curve

p	1	5	10	15	20	30	40	50	60	65	70	72.9
T	(193.5)	216.2	233.4	245.05	254.1	268.15	279.0	288.0	295.7	299.15	302.35	304.1
μ_v	(3.055)	2.510	2.135	1.922	1.773	1.545	1.371	1.211	1.043	0.937	0.801	0.6050
μ_l	(?)	−0.0346	−0.0083	−0.0031	0.0046	0.0245	0.0575	0.1182	0.2225	0.2985	0.418	0.6050

T	216.9	220.0	230.0	240.0	250.0	260.0	270.0	280.0	285.0	290.0	295.0	300.0
p	5.15	5.95	8.8	12.65	17.6	23.9	31.55	41.0	41.0	52.55	59.0	61.3
μ_v	2.475	2.410	2.200	2.020	1.841	1.675	1.515	1.354	1.354	1.174	0.961	0.914
μ_l	−0.3375	−0.0290	−0.0167	−0.0074	+0.0007	+0.0115	0.0285	0.0625	0.0938	0.1386	0.2095	0.3235

Values below correspond to regions of rapid rates of charge of μ along isotherms.

T	220.0	230.0	304.1	304.1	304.1	304.1	304.1	310.0	310.0	315.0	315.0	315.0
p	5.0	5.0	70.0	72.0	74.0	76.0	90.0	85.0	90.0	85.0	90.0	95.0
μ	2.387	2.132	0.822	0.767	0.382	0.310	0.159	0.360	0.250	0.569	0.443	0.312

ON THE THERMODYNAMICS OF THERMAL TRANSPIRATION AND OF THE THOMSON EFFECT

By E. H. Kennard

Abstract

Thermodynamics of thermal transpiration.—One can obtain an apparent violation of the Second Law by means of thermal transpiration, constructing an engine with an apparent efficiency of 50 per cent for small ranges of temperature. But in reality the thermal effusion of a gas and the conduction of heat through it are merely two aspects of a single process and when the degradation of heat due to conduction is taken into account the apparent violation disappears.

Thermodynamics of the Thomson effect.—An analogous phenomenon in connection with the diffusion of electrons in a metal requires a slight modification of the formula obtained for the Thomson effect from the electron theory; the thermo-electric law deduced from equilibrium thermodynamics is then found to hold only because these effects in the two branches of the circuit cancel each other. If the current in reality is not carried entirely by electrons, or if one branch of the circuit is made to consist of an electron gas, then the effect should become noticeable. Hence conclusions drawn from equilibrium thermodynamics in such cases must be regarded as essentially tentative.

IN applying thermodynamical laws to thermo-electricity it has been usual to ignore the degradation of heat caused by thermal conductivity on the ground that this process was presumably quite independent, from the thermodynamic standpoint, of the mechanism by which the thermal e.m.f. is set up. Misgivings in regard to this assumption have often been expressed, but one important positive reason for regarding it as questionable seems to have been overlooked.

Thermodynamics of Thermal Transpiration

The consideration in question stands out in full view in the case of a perfect gas at low pressure undergoing thermal transpiration through a porous partition. Experiment and Kinetic Theory both show that, if the absolute temperatures of the gas are T_1 and T_2 on the two sides of the partition, the pressures p_1 and p_2 take on steady values given by

$$p_1^2 T_2 = p_2^2 T_1. \qquad (1)$$

Supposing now that $T_1 > T_2$, let us carry a gram of gas through a cycle thus: Let us withdraw it from the compartment at T_1, cool it at constant volume to T_2, compress it at constant temperature to p_2, force it into the

compartment at T_2, and finally allow it to flow back into the other compartment through the partition; and let us consider the thermodynamic aspects of this cycle.

Work is done by the gas in three parts of the cycle. Since the cooling reduces the pressure from p_1 to p_1T_2/T_1, the work during compression to p_2 is $-RT_2 \log (P_2T_1/p_1T_2)$ or, from Eq. (1), $-RT_2 \log \sqrt{(T_1/T_2)}$, R being the gas constant for one gram; hence the total external work done by the gas is

$$W=R(T_1-T_2)-\tfrac{1}{2}RT_2 \log (T_1/T_2). \qquad (2)$$

On the other hand, the heat given out by the gas in cooling is exactly offset by the heat that must be supplied in the partition during the last stage to raise the temperature of the gas as it flows through; but additional heat of amount $H=R(T_1-T_2)$ must also be furnished during the last stage to provide energy for the difference in the pv work on the two sides of the partition.

Thus we have an engine absorbing heat H at a temperature ranging from T_2 to T_1 and doing work W. Its efficiency is $n=W/H$ or

$$n=1-\frac{T_2}{2(T_1-T_2)} \log \frac{T_1}{T_2} \qquad (3)$$

For *small* values of (T_1-T_2) this efficiency is approximately independent of the temperature-difference and equal to 50 per cent.

We should thus have a beautiful device for violating the Second Law, were it not for the degradation of heat brought about by conduction through the gas in the partition. The latter process cannot for a moment be separated in thought from the process by which the difference in pressure is maintained, for it is the same process of molecular diffusion which carries molecules in excess toward the hot side and thermal energy in excess toward the cold; the difference of pressure is really only a by-product accompanying the conduction of heat.

In qualitative confirmation of this explanation we may note that if the transpiration of the gas were determined merely by the difference in pressure as in an isothermal process, then the pressures would become equal on both sides of the partition, the factor $\frac{1}{2}$ would disappear from the second term in (2) and in (3), and the efficiency n would vanish with (T_1-T_2), in harmony with the laws of equilibrium thermodynamics. The peculiarity of the actual phenomenon arises from the fact that the process of molecular diffusion tends to establish equality not of pressure but of the quantity $p\sqrt{T}$.

It may be of interest to show that the compensation by conduction is adequate by showing that the resulting loss of free energy necessarily exceeds the maximum work obtainable from a transpiration engine

such as we have described. We shall do this only for a simple case in which the molecular distribution certainly approximates closely to Maxwell's, namely, the case where the partition is very thin and is impermeable to heat but sprinkled with holes much less in diameter than the length of the mean free path of the gas.

Let μ_{12}, μ_{21} denote the rates of effusion of gas in grams per unit area per second from side 1 to side 2 of the partition and vice versa, respectively. Then the power developed by the engine is $P_t=(\mu_{21}-{}_1\mu_2)W$, so that, by (2), $P_t<R(T_1-T_2)\ (\mu_{21}-\mu_{12})$. The power obtainable thermodynamically from the heat H, which must here be supplied at temperature T_1, is $H\ (\mu_{21}-\mu_{12})\times(T_1-T_2)/T_1$; subtracting this from P_t and inserting the value of H, we have for the power not accounted for by the reversible heat-supply

$$P_t'<R(\mu_{21}-\mu_{12})\ (T_1-T_2)\ (T_2/T_1). \tag{4}$$

But the usual law of effusion [cf. Eq. (318) in Jeans' Dynamical Theory of Gases, 3d ed.], $\mu_{12}=bp_1/\sqrt{T_1}$, $\mu_{21}=bp_2/\sqrt{T_2}$, where $b=1/\sqrt{(2\pi R)}$. To make the power positive we must have $p_1>p_2$, hence $\mu_{21}-\mu_{12}<\mu_{12}[\sqrt{(T_1/T_2)}-1]$; then (4) gives (provided $T_1>T_2$)

$$P_t'<R\mu_{12}(T_1-T_2)^2/2T_1. \tag{5}$$

For comparison, we will calculate the accompanying flo of heat energy in terms of the flow of mass. The density of mol cules with speeds between c and $c+dc$ being by Maxwell's Law $Ac^2e^{-hmc^2}\,dc$, where m is molecular mass and h and A are independent of c, the number of such molecules passing across unit area of a hole per second will equal this expression multiplied by c and by a geometrical factor β (due to obliquity of motion), and since each molecule carries heat energy of amount $\frac{1}{2}\alpha mc^2$, where α is a constant not less than unity, the total rate of transfer of heat energy per unit area from side (1) to side (2) will be

$$\Gamma_{12}=\tfrac{1}{2}A_1\alpha\beta m\int_0^\infty c^5e^{-h_1mc^2}dc,\ =\frac{A_1\alpha\beta}{h_1}\int_0^\infty c^3\ e^{-h_1mc^2}dc$$

after an integration by parts. But the rate of transfer of mass is, similarly,

$$\mu_{12}=A_1\beta m\int_0^\infty c^3e^{-hmc^2}dc.$$

Hence
$$\Gamma_{12}=\alpha\mu_{12}/h_1m, \text{ or, since } h_1=1/(2mRT_1), \tag{6}$$
$$\Gamma_{12}=2RT_1\alpha\mu_{12};\ \Gamma_{21}=2RT_2\alpha\mu_{21}.$$

Under equilibrium conditions where $\mu_{21}=\mu_{12}$, the net flow of heat energy, $\Gamma_{12}-\Gamma_{21}$, represents a transfer by conduction; if this heat were transferred reversibly the power obtained would be

$$P_e=(\Gamma_{12}-\Gamma_{21})(T_1-T_2)/T_1=2R\alpha\mu_{12}(T_1-T_2)^2/T_1. \tag{7}$$

If $\mu_{21} > \mu_{12}$, we can regard the difference as simply a superposed molar current of gas. Thus P_c as given by (7) represents in the general case the rate of loss of free energy by conduction.

Comparing (5) and (7) we see that $P_t' < P_c$ by an ample margin.

Thermodynamics of the Thomson Effect

It is clear from the preceding discussion that differences of pressure due to thermal transpiration cannot be treated thermodynamically as an equilibrium phenomenon; yet the Thomson effect, which is usually ascribed to a sort of thermal transpiration of the electrons, has commonly been so treated and the conclusions reached have not been contradicted by experiment.

We can get a general idea of what is to be expected in the Thomson case by considering the following simple modification of the old electron theory.

The free paths of the electrons being supposed practically independent of temperature, the number colliding with an atom within a given element of volume and then crossing unit area of a plane drawn normal to the temperature gradient will be proportional to the electronic density n and to the mean speed or to $\sqrt{T}$, and the flow of electrons in one direction to diffusion will thus be proportional to the gradient of $n\sqrt{T}$. In a state of equilibrium this flow is offset by a flow produced by an electric potential gradient; hence, if V = potential, γ = conductivity, x = distance in direction of temperature gradient, we can write for the state of equilibrium

$$\gamma \frac{dV}{dx} = -a \frac{d}{dx}(n\sqrt{T}). \tag{7}$$

Now when T is uniform this equation must lead to the familiar value for the Peltier difference of potential between two metals, viz., $V_1 - V_2 = -kT/e \log(n_1/n_2)$,[1] k being the gas constant for one electron and e, the electronic charge; if we put $a = \gamma k\sqrt{T}/ne$, Eq. (7) gives

$$e\,dV = -(k\sqrt{T}/n)d(n\sqrt{T}) \tag{8}$$

and yields the value of $V_1 - V_2$ just stated, by integration with T constant.

The Peltier coefficient Π_{12}, measured as heat given out when unit charge passes from metal 1 to metal 2, is then equal to the drop in potential from the first metal to the second or to $V_1 - V_2$, so that

$$\Pi_{12} = (kT/e)\log(n_2/n_1). \tag{9}$$

The Thomson coefficient σ, measured as heat absorbed when unit charge passes to a point where the temperature is higher by 1°, equals $dV/dT +$

[1] Cf. K. Baedeker, Elektrische Ersch. in met. Leitern, p. 89, Eq. (2); J. Kunz, Phil. Mag. **16**, 767, 1908

$(3/2)k/e$, the first term being the work done against the electric field and the second, the internal specific heat of the electrons regarded as a monatomic gas; whence, by (8),

$$\sigma = -\frac{kT}{en} \cdot \frac{dn}{dT} + \frac{k}{e}. \tag{10}$$

The equation given by thermodynamics and by experiment,

$$T\frac{d}{dT}\left(\frac{\Pi_{12}}{T}\right) = \sigma_1 - \sigma_2 \tag{11}$$

is obviously consistent with (9) and (10). But this holds partly because the second term in the value of σ is the same for all substances and cancels out on the right side of (11); since this term includes the effect of the factor $\sqrt{T}$ in $d(n\sqrt{T})$ in (8), which can be regarded as the transpiration effect, we may say that the conclusions reached from equilibrium thermodynamics hold simply because the transpiration effects in the two branches of the circuit balance out. (This term in σ is usually omitted nowadays, partly for the good reason that the specific heat of the electrons seems to be small, and partly because the direct effect of the temperature gradient upon diffusion is usually overlooked and only the gradient of electronic density is considered,[2]—but the direct temperature effect has been taken account of in connection with metallic conductivity by E. H. Hall.)

When the true theory of conductivity shall have been discovered, it is possible that this compensation will not be perfect; for instance, if, as in the theory of E. H. Hall, the atoms somehow carry part of the current, the second term in σ may vary with the material and (11) may then be found to be not always or only approximately true. Again, when one branch of the circuit consists of an electron gas and this is subjected to a reversible process while thermal conduction has free play in the other branch, as in some of Richardson's arguments, then such an effect may be expected to come to light.

Clearly results obtained by thermodynamic reasoning in which systems involving temperature gradients are treated as if they were in equilibrium must be regarded as being tentative or hypothetical in nature and as requiring confirmation by experiment.

CORNELL UNIVERSITY,
July 5, 1923.

[2] Cf. J. Kunz, loc. cit.[1]

A DIRECT MEASUREMENT OF POLARIZATION CAPACITY AND PHASE ANGLE

By Carl W. Miller

Abstract

Polarization capacity and phase angle of electrolytic cell having gold electrodes and potassium bromide as electrolyte.—Using symmetrical condensers in which the separation of the plates could be varied from .002 cm to .3 cm, the series resistance and the capacity for small current density were measured by means of an alternating current bridge. Within the errors of the experiment, the "initial" capacity was independent of the separation of the plates, and the resistance was a linear function of the separation, approaching, however, a definite surface resistance as the distance between the plates was reduced. For concentrations greater than hundredth normal it was possible to work with such small separations that the resistance of the electrolyte could be neglected in comparison with the surface resistance. Direct measurements were, therefore, possible of capacity, resistance, and phase angle ($\tan^{-1}\omega CR$). Using clean gold electrodes as soon as possible after immersion in the electrolyte, a study was made of the variation of these constants with concentration, and for a few frequencies from 570 to 3500 cycles. The capacity varied very nearly directly and the resistance inversely as the one-fourth power of the concentration, the product CR being nearly constant. The phase angle was very nearly constant for variations both of concentration and of frequency, showing only a slight decrease with increasing concentration, and a slight increase with increasing frequency. It was about 65°.

Introduction

It has long been known that the polarization capacity of an electrolytic condenser decreases as the current passing through decreases, but approaches a limiting so-called "initial" capacity. Measurements of this initial capacity have been made by Wien, Krueger, Warburg, and others, while a number of theories have been proposed to explain the observed phenomena.

Related to the polarization capacity is the dissipation of energy at the surface of the condenser plate which is evidenced by the apparent increase in the resistance of the condenser over and above the calculated resistance of the electrolyte. Hitherto, estimates of this surface resistance have been made by comparing the observed series resistance of the condenser with that to be expected from the nature and dimensions of the electrolyte. In case the condenser used was unsymmetrical and this could not be done, a less certain estimate was still possible from the variation of capacity and resistance with frequency.

Experimental Procedure

In the measurements here described symmetrical condensers have been used, but the surface resistance has been determined by a study of the variation of capacity and resistance as the separation of the plates was progressively decreased. By this method I have been able with all but the most dilute solutions to bring the plates so close together as to render the resistance of the electrolyte itself negligible. The disadvantage of this procedure is that it unavoidably confuses the quite different processes which are probably going on at a given instant at the two plates. We may think of the cell as made up of two identically equal leaky condensers in series with one another and with the electrolyte. We must, however, not lose sight of the fact that this conception may be very far from representing the processes which are actually taking place.

Practically all previous measurements have been made on cells which have been assembled for at least twenty-four hours. This has been rendered necessary by the constant changes which take place at the surface of the plate after it is immersed in the electrolyte. These changes are quite rapid at first, and persist for many hours, thus rendering consistent measurements difficult. We are, of course, somewhat in doubt as to the exact nature of the metallic surface after such a prolonged immersion.

The measurements described in this paper were, on the other hand, made as soon as possible after the electrodes were brought into contact with the electrolyte. Considerable care has been exercised in cleaning the metal surfaces used, and the results show, at least approximately, what is to be expected from a clean metal surface in contact with a clean electrolyte. Since the cell was changing relatively rapidly, it has, of course been impossible to make series of measurements with the precision attainable after long immersion.

An alternating current bridge was used. The two balancing arms were 1000 ohm non-inductively wound resistances, the third arm contained a variable capacity and resistance which could be used either in parallel or in series, while the fourth arm contained the electrolytic condenser to be studied. Provision was made for substituting in place of the electrolyte a second variable capacity and resistance for the purpose of direct comparison, so as to eliminate any possible error which might arise from inequality of balancing arms or leakage of current from capacitance to ground. The disadvantage of this method was its cumbersomeness, and during a part of this work the same purpose was served, though less satisfactorily, by a device, due to Wagner, through which the midpoint

of the bridge was maintained at ground potential without any actual ground connection. A two stage tuned amplifier was used in the telephone circuit to increase the sensitiveness of the apparatus.

Two types of symmetrical condenser were devised which proved particularly useful in these measurements. The first and simplest consisted of a micrometer caliper to the anvil of which had been cemented an insulated brass cylinder 1 mm thick and, like the anvil, one-quarter inch in diameter. This disk and the opposing face of the movable spindle were gold plated, and together constituted the condenser. All except the opposing faces were covered with an insulating coat of shellac, and a single drop of electrolyte was held between the plates by capillarity. One lead was brought to the brass cylinder and the other to the frame of the caliper. It was possible to bring the plates of this condenser to within .002 mm of one another without shortcircuiting. The plates could be readily cleaned and polished, and one drop of electrolyte could be conveniently replaced by another. It was, of course, not suited to long series of observations owing to gradual changes in concentration consequent on evaporation.

The other type of condenser consisted of two circular opposing disks, the separation of which could be controlled by a micrometer screw. All except the front faces of the disks and the leads were carefully insulated so that they could be immersed in a beaker of electrolyte without permitting any conduction except between the opposing faces. The difficulties resulting from evaporation were eliminated by this arrangement, but the simplicity and convenience of the caliper condenser were to a certain extent sacrificed.

Effect of Changing the Separation of the Plates

The following table shows a series of measurements made with the immersion condenser. The plates were gold plates, and a 1/500 normal solution of KBr was the electrolyte. An alternating current of 3400 cycles was furnished by a vacuum tube oscillator.

t:	.10	.15	.20	.25	.30	.10 mm
R:	9.662	12.91	16.22	19.73	23.16	9.86 ohms
C:	6.57	6.52	6.56	6.55	6.68	6.65μ-farads

t is the separation of the plates in millimeters, R is the series resistance of the condenser in ohms, and C is the series capacity in microfarads. C remains satisfactorily constant, indicating that its seat is at the surface of the metal and not in the electrolyte. R is plotted in the large curve of Fig. 1 against the separation. It is quite accurately linear, and clearly approaches a limiting value of about 3 ohms as the separation approaches

zero. The slope of this line is 675 ohms per cm separation. The plates were one inch in diameter, and the molecular conductivity would then be

$$\Lambda = \sigma/\eta = [.02/13.5 \times \pi(1.27)^2\ 2(10)^{-6}] = 146$$

Calculating Λ from the sum of the mobilities of the bromine and potassium ions, and from the degree of dissociation for a five-hundredth normal solution, we get $\Lambda = 128$. The check would seem to be as good as could be expected.

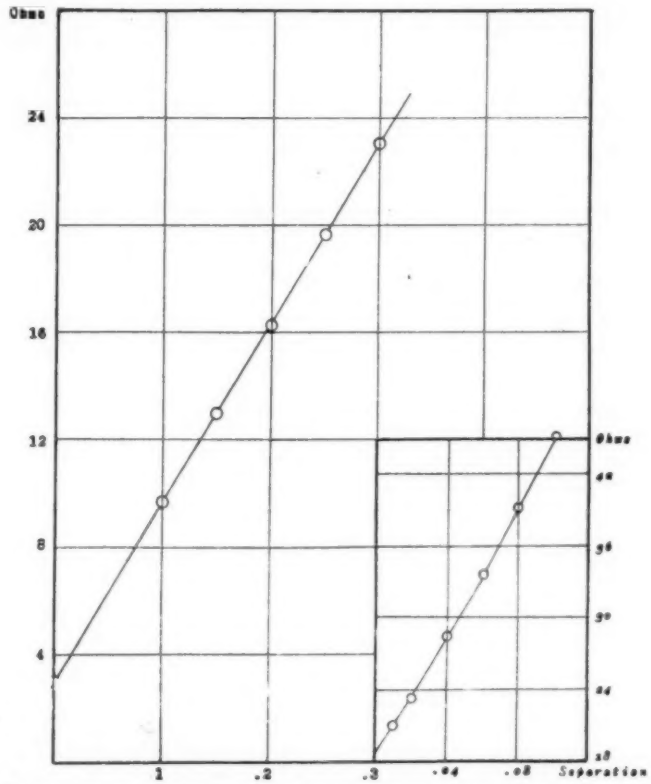


Fig. 1. Series resistance as a function of separation of the plates.

The following data are for a similar series of measurements made with the caliper condenser. A .001 normal solution of KBr was used, and a 3500 cycle current. The lack of constancy of C and the lack of exact linearity in the variation of R is to be attributed to the gradual evaporation of the electrolyte.

t:	.10	.08	.06	.04	.02	.01	.10 mm
R:	45.3	39.3	33.4	28.4	23.3	20.9	39.2 ohms
C:	.668	.698	.723	.746	.768	.793	.735 μ-farads

These values of R are plotted against t in the insert of Fig. 1. The limiting resistance as t approaches zero is here seen to be about 18.7

ohms. It is clear that for this .001 normal solution, the resistance of the electrolyte alone at .003 mm separation is very nearly negligible compared to the surface resistance; for higher concentrations it is of still less importance.

Effect of Changing the Concentration of the Solution

Using the caliper condenser and a separation of between .002 and .003 mm, a large number of measurements were made with several different electrolytes, KBr, Na_2CO_3, $AgNO_3$. The following results with KBr are typical of all these measurements.

The instant a drop of solution was placed between the jaws of the caliper a stop clock was set into operation. A balance was obtained as quickly as possible on the bridge, and readings made of capacity, resistance, and time. These measurements were repeated at intervals over a period of ten to fifteen minutes, after which the plates were again cleaned and a new set of readings begun.

The results are indicated in Table I for three different concentrations and a 2500 cycle current. The current density was in all cases

Table I

Concentration	Time (min.)	Resistance (ohms)	Capacity (μ-farads)	tanφ
.01 N	1:00	143	.983	2.21
	3:00	140	1.039	2.24
	5:30	136.2	1.076	2.30
	8:00	133.2	1.096	2.30
	10:30	130.5	1.120	2.30
	——	127.5	1.135	2.28
.1 N	:50	82.7	1.659	2.16
	3:00	75.6	1.819	2.16
	5:00	72.5	1.884	2.15
	6:50	71.0	1.914	2.14
	9:30	70.2	1.934	2.14
	12:00	70.4	1.934	2.14
1.0 N	1:05	35.9	3.564	2.02
	2:35	36.2	3.582	2.04
	4:15	36.7	3.555	2.05
	6:30	37.7	3.481	2.06
	8:50	38.6	3.423	2.08
	11:00	39.1	3.389	2.08

between one and two milliamperes per cm, and we are accordingly dealing with the "initial" capacity.

It will be noted that at the two lower concentrations the resistance decreases with the time, while the capacity increases. At the highest concentration, however, the resistance increases and the capacity de-

creases. In all three cases RC and hence the phase angle stays nearly constant. Furthermore, despite the great range of concentrations, this phase angle does not differ much in the three cases.

The variation of C and R individually with concentration is not so easy to estimate, owing to the rapid changes which take place with the time. If, however, we compare the values of C and R which correspond to the same length of time after immersion, it is readily seen that C varies very nearly directly and R inversely as the one-fourth power of the concentration.

It is interesting to compare this one-fourth power law with the observations of previous investigators. Warburg's theory for reversible electrodes requires that C shall increase in direct proportion to the first power of the concentration, and this law was verified by Neumann. Wien, on the other hand, found a very slow rate of variation of C with the concentration in the case of nickel, much slower, in fact, than we have observed with gold. It is worthy of note, however, that the phase angle we have found for gold, 65°, lies well between the 45° characteristic of reversible electrodes and the 82° found by Wien for nickel. There would seem, therefore, to be a very intimate connection between the phase angle and the rate of variation of the capacity with the concentration.

Effect of Changing the Frequency of the Applied Current

A range of frequencies from 570 to 3500 cycles was available for these measurements, and the following table gives four different pairs of observations obtained at different times over a period of several months. The differences observable must be attributed to differences in the condition of the condenser plates. In each case, however, the plates had been subjected as nearly as possible to the same process of cleaning and polishing, and the disturbing causes are not understood.

Concentration:	.1 N	.1 N	.1 N	.1 N	.01 N	.01 N	.01 N	.01 N
Frequency :	3500	2000	3500	2270	3500	2700	1040	570
Resistance :	8.18	10.4	9.5	12.0	20.4	21.7	50.3	91.1
Capacity :	2.458	3.554	2.040	2.532	.894	1.071	1.457	1.66
tan φ :	2.27	2.16	2.35	2.31	2.49	2.47	2.09	2.06

It is to be noted that in all cases both R and C decrease as the frequency increases, but in such a fashion that the phase angle remains very nearly constant. There would appear, however, even with the small range of frequencies available, to be a slight increase in the phase angle with increasing frequency. These variations are, however, of an entirely different order of magnitude from the variations of C and R.

The recurrence of this curious constancy of the phase angle both as regards variations of concentration and frequency would seem to be highly significant. Any thoroughgoing theory must give an adequate explanation of this phenomenon.

These measurements were carried out during the spring and summer of 1922 in the Cruft Laboratory of Harvard University.

NEW YORK UNIVERSITY,
May 22, 1923.

THE CHANGE IN THE ELECTROMOTIVE FORCE BETWEEN A METAL PLATE AND A SOLUTION ON BEING SUDDENLY BROUGHT INTO CONTACT

By R. D. Kleeman and R. H. Bennett

Abstract

Electromotive force between a metal plate and a solution.—One plate immersed in a solution was connected through a D'Arsonval galvanometer to another plate of the same metal and the deflection of the galvanometer was observed when the second plate was plunged into the solution. In some cases, e.g., Zn in water or in a solution of $ZnCl_2$ or of $ZnSO_4$, the initial deflection was in the direction to be expected from the equilibrium difference of potential between the plate and the solution, but was followed by a deflection in the reverse direction. In other cases, e.g. Cu, Ni, Al, Fe, Mg, Pt and Sn in water, the initial deflection was in the reverse direction. These reverse deflections seem to be due to the production of an initial difference of potential which is greater than the equilibrium potential and which then oscillates about the equilibrium. This indicates that the process of establishing a difference of potential between a metal plate and a solution possesses marked *inertia*. The results are in agreement with the transition layer theory of the e.m.f. of a cell recently suggested by Kleeman.

WHEN a metal plate is immersed in a solution the formation of the difference of potential between them will obviously be a function of the time. It is also highly likely that it would possess the property of inertia. This would evidently be, if it exists, the more conspicuous the shorter the time of formation of the difference of potential. This property follows immediately from a theory of the e.m.f. of a cell given previously,[1] as will be shown at the end of the paper. These considerations led to the following experiments being undertaken.

Two metal plates A and B of the same material were connected to the binding posts of a D'Arsonval galvanometer, the plate A being immersed in a solution and the other plate B suspended above it. On suddenly plunging the suspended plate B into the solution a deflection was obtained whose nature depended on the rate and character of formation of the e.m.f. between the plate and the solution. Readings were taken immersing the suspended plate several times in succession, and also drying it and cleaning it with fine sandpaper before each immersion. Since there is usually a small difference of potential between two plates of the same material in a solution, readings were also carried out with the plates interchanged. The deflections obtained were usually much larger than

[1] R. D. Kleeman, Phys. Rev. **20**, 174 (1922)

the constant deflection ultimately obtained under conditions of equilibrium. Occasionally it was necessary to put several thousand ohms in the galvanometer circuit to prevent the deflection being off the scale. The sensitiveness of the galvanometer was about one mm scale deflection for 10^{-6} volt.

If the e.m.f. is formed very slowly, the initial galvanometer deflection will correspond to a current flowing from the stationary plate *A* through the galvanometer if this plate is positive with respect to the solution, and vice versa. This flow would be assisted by the increase in electrostatic capacity of the plate suddenly immersed.

The combinations of metals and solutions given in Table I behave in the foregoing way. The third column gives the electrical charge which the plate suddenly immersed appears to assume with respect to the

TABLE I

Metal	Solution	Apparent charge on *B* with respect to A	Charge on plate with respect to solution	Reversals
Cd	Water	—	+	—
Zn	Water	+	—	R
Mo	Water	+	—	R
Zn	2% zinc chloride	+	—	R
Zn	2% zinc sulphate	+	—	R
Cu	2% copper sulphate	—	+	

other plate, the fourth column gives the charge on the plate with respect to the *solution* under conditions of equilibrium, and the fifth column indicates by R when a galvanometer deflection was followed by a marked deflection on the other side of the zero.

A deflection followed by a deflection in the reverse direction indicates that the difference of potential between the solution and the plate suddenly immersed, temporarily increased beyond that corresponding to the condition of equilibrium. This effect shows that the process of formation of the difference of potential possesses inertia.

Table II gives the combinations of metals and solutions for which the difference of potential between plate and solution is formed so rapidly that the initial current due to the formation of the difference of potential up to the value corresponding to the condition of equilibrium, is not observed on account of the inertia of the galvanometer coil. In these cases there appears instead a current in the reverse direction due to a temporary increase of the difference of potential beyond that corresponding to the condition of equilibrium. This will appear from a comparison of the third and fourth columns of the Table. The sign of the electric

charge on a plate with respect to the solution when it was water, was obtained from previous experiments,[2] and in the case of a solution of a salt, from Winckelmann's Handbuch der Physik, II ed.

These results show in a striking way that the process of formation of the difference of potential between a plate and a solution when suddenly brought into contact with each other, possesses inertia. It seems likely from the results obtained that the difference of potential oscillates about that corresponding to equilibrium, with decreasing amplitude for a time. A decrease of the difference of potential below that of equilibrium from a temporary decrease above it, was observed in the case of tungsten and distilled water. This effect would be observed in those cases only when

TABLE II

Metal	Solution	Apparent charge on B with respect to A	Charge on plate with respect to solution
Cu	Water	—	—
Ni	Water	—	—
Al	Water	—	—
Fe	Water	+	+
Mg	Water	—	—
W	Water	—	—
Pt	Water	—	—
Sn	Water	—	—
Cu	2% sol. of copper nitrate	+	+
Cd	2% sol. of cadmium nitrate	—	—

the period of oscillation of the difference of potential corresponded approximately to the period of oscillation of the galvanometer coil, which was several seconds.

There are some cases lying between the two considered in which a current in one direction is succeeded by an equal current in the opposite direction with such rapidity that practically no galvanometer deflection should be obtained; actually, galvanometer deflections are obtained, but they are as likely to be in one direction as in the opposite. This is probably due to the fact that the values of the deflections obtained depend somewhat on the rapidity with which the suspended plate is immersed. Lead plates in water appear to be a combination of this kind.

Table III gives some results obtained with combinations for which the nature of the potential of plate with respect to the solution is not known. When this information is available it will be possible to determine to which category each combination falls.

[2] Kleeman and Fredrickson, Phys. Rev. **22**, 134, 1923

The experiments described are of a preliminary nature. It is intended to continue them, using an oscillograph, when one is available, to ascertain if possible the period of oscillation of an e.m.f. during its formation.

The foregoing results fall into line with a theory of the e.m.f. of a cell proposed previously.[1] According to this theory the difference of potential between a metal plate and a solution with which it is in contact, is caused by a layer of segregated ions adjacent to the plate. This segregation is caused by differences in velocity, rate of diffusion, and rate of production of ions, in different parts of the layer, due to changes in density from one side of the layer to the other. The segregated layer of ions gives an electric charge to the plate, of the same sign as that of the ions in surplus close to the plate, and therefore under conditions of equilibrium the

TABLE III

Metal	Solution	Apparent charge on B with respect to A
Fe	1.5% sol. of ferrous sulphate	+
Cu	2% sol. of cupric chloride	—
Pb	Saturated sol. of lead sulphate	+
Pb	Saturated sol. of lead chloride	—

e.m.f. between the plate and solution is equal to the e.m.f. due to the charge on the plate and an equal and opposite charge on the solution, and that due to the segregated ions in the layer. Now when a plate is brought into contact with a solution, a change in density of the layer next to the plate will suddenly take place. The inertia of the process will carry it beyond the state of the layer corresponding to conditions of equilibrium, and this will necessarily be followed by a partial reversal of the process, and so on. The sudden change in the density of the layer would give rise to a sudden change in the dissociation of molecules into ions, and in the recombination of ions. These processes would also possess inertia, since they involve the displacement of matter. Similar remarks apply to the diffusion of ions from one part of the layer to another which is continually going on.

No other theory of the e.m.f. of a cell appears to give a satisfactory explanation of the effects observed.

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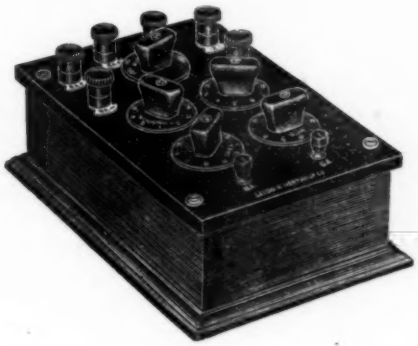

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Suggestions as to content. On account of the high cost of printing, brevity is of great practical importance. Historical summaries of previous results and also discussions which consider various possible explanations without leading to definite conclusions, should be made very brief, except in special cases. The greater part of the paper should be devoted to the actual new results and to a concise presentation of the conclusions to which they lead. Attention should be directed to the more accurate and more conclusive experiments, omitting any which add nothing. The amount of detail included should be governed somewhat by the importance of the results and their interest to physicists.

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Abbreviations. Omit periods after such symbols for units as the following: cm, mm, kv, lb, A, °C; also after I, II, . . . and per cent, and after headings in columns in Tables. Write a.c., d.c., e.m.f., abscissas, disk, in vacuum, wave-length, x-rays. Refer to figures as Fig. 1, Figs. 3 and 4; and to equations as: Eq. (5); Eqs. (7) and (8).

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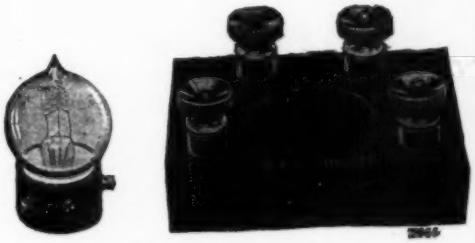

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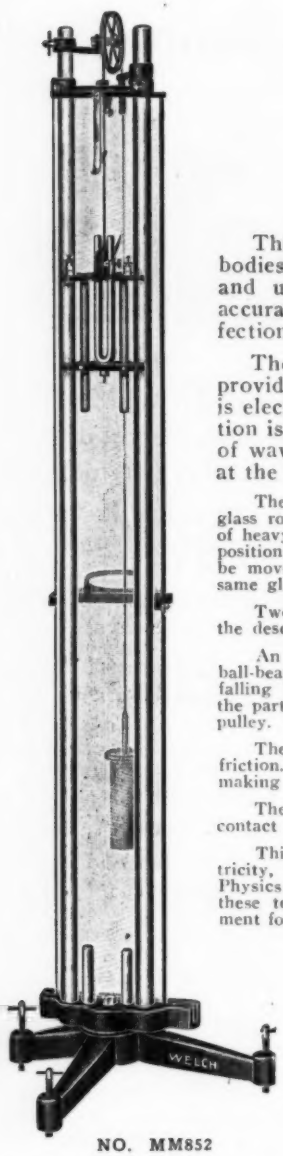

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The form of the abstract which has been used for the past three years in the REVIEW is the analytic abstract developed by the National Research Council. While we hope authors will try to put their abstracts in this form, which is not at all difficult, we will accept abstracts in the ordinary form, if they are otherwise adequate, and will make what changes are needed in this office.

In the preparation of analytic abstracts, the best procedure is as follows:

1. *Notes.*—Read the article carefully, analyzing the information contained and taking notes covering all the new information reported.

2. *Subtitles.*—Write, first, a title describing the group of results forming the main contribution of the article, including all that belong together. If there are in addition results which do not come under that title, gather them into as few groups as possible and formulate a complete and precise title for each group. For examples see the subtitles, in bold face and italics, in the abstracts in current numbers of the REVIEW. The subtitles should together form a complete index of the new information. They should be formulated before the text is written.

3. *Text.*—Write a paragraph adequately summarizing the main group of results and including the corresponding subtitles, and then do likewise for the other groups. A separate paragraph should be used for each distinct subject involved, but all material which can easily be grouped together under a single title should be summarized in the same paragraph. Parts of subtitles may be scattered through the text, but the subject of each paragraph must be given at the beginning. Italicize subtitles but no other words or phrases.

4. *Final Checking.*—Re-read the article so as to check the abstract, and correct any omissions and mistakes; read the subtitles by themselves to see that they properly index the information; and read the abstract to see whether it cannot be condensed and its English be improved. The abstract should be made as readable as the necessary brevity will permit.

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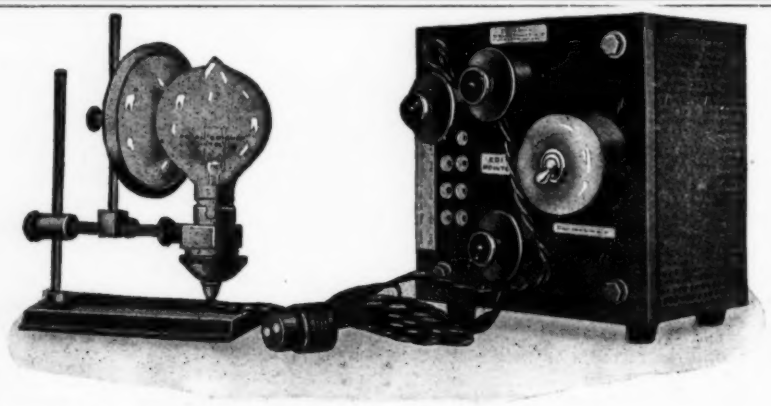

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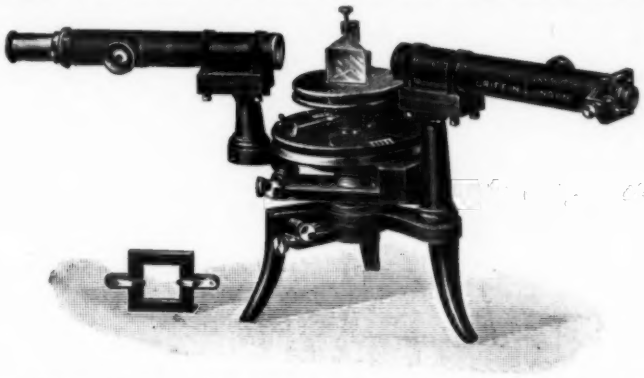

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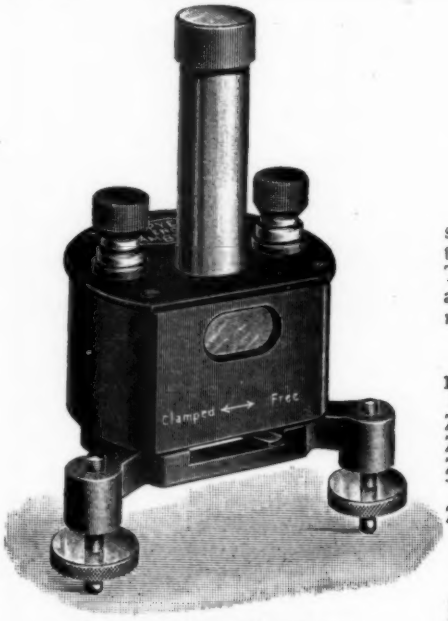

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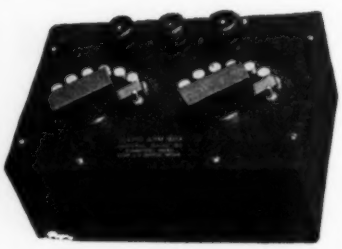

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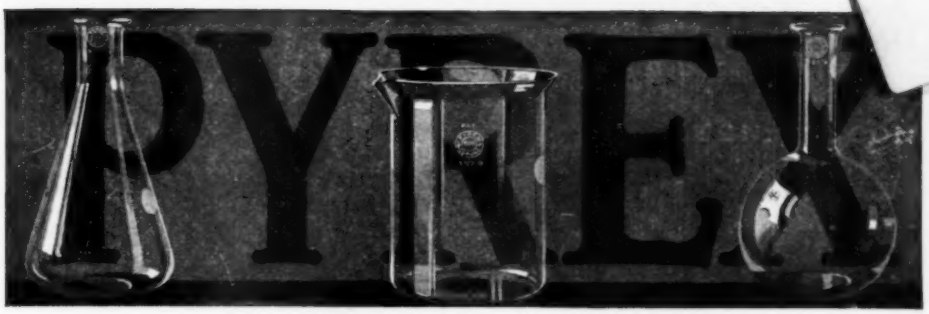

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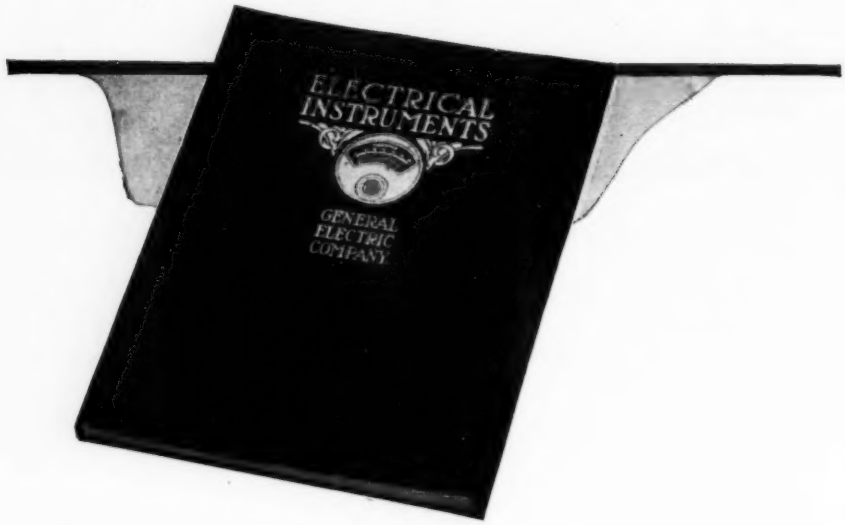

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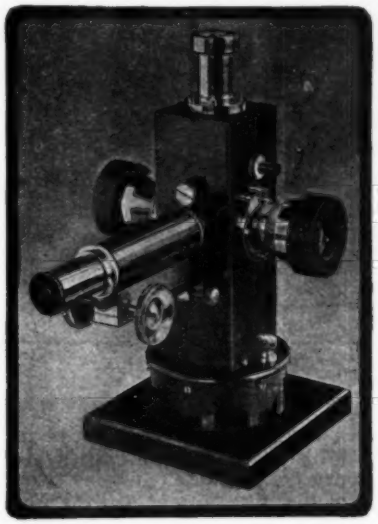

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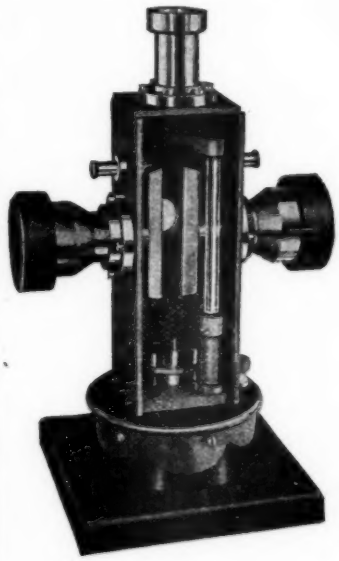

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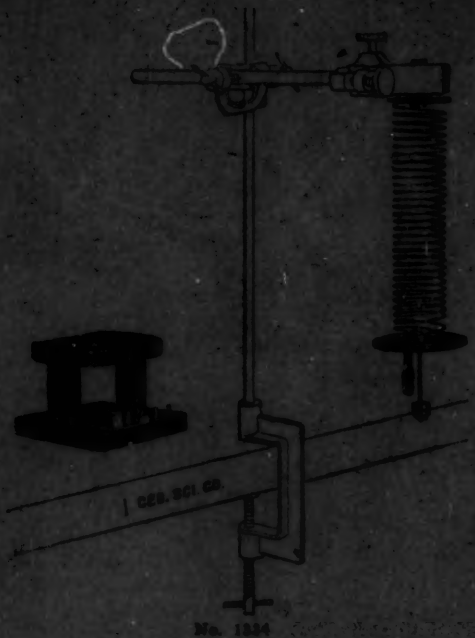

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